THE CRYSTAL STRUCTURE OF QUINOL DIMETHYL ETHER.

ADDITIONAL PAPER: THE CRYSTALLITE ORIENTATION IN DIFFERENT GRADES OF MANILA AND SISAL FIBRES.

THESIS

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SUMMARY.

The crystal and molecular structure of quinol dimethyl ether has been determined by quantitative two-dimensional X-ray methods. The crystals are orthorhombic bipyramidal and belong to the Pbca space group. There are four molecules per unit cell and each molecule possesses a centre of symmetry which coincides with the crystallographic centre of symmetry. The molecular planes are inclined at about 33° to the (100) plane. The methyl group is not rotating and is coplanar with the rest of the molecule. The benzene ring is considerably distorted with the bond lengths varying from 1.36 A.to 1.44 A. The length of the bond connecting the methyl group to the oxygen atom is 1.35 A. All valency angles are about 120°. The hydrogen atoms of the methyl group are also in fixed positions. There is no intermolecular distance smaller than 3.5 A. These determinations should be accurate to within ±0.02 A. or ±0.03 A. The above results are supported by good structure factor agreements and by theoretical considerations of the possible resonance structures. The benzene ring bond which is "trans" to the methyl group is only 1.36 A. long and a qualitative explanation of this has been put forward.

INTRODUCTION.

Professor J. M. Robertson determined the axial lengths and the space group of quinol dimethyl ether and his results indicated that this compound would be suitable for a detailed X-ray analysis.

Since no attempt had been made to investigate the structure of any of the aromatic ethers by means of X-rays, a quantitative X-ray investigation of 1:4 dimethoxybenzene appeared to be of great importance and was therefore undertaken.

Its value lay in the fact that it was expected to throw light on many structural aspects of this compound, which had remained purely speculatory and that it would greatly facilitate possible future analyses of other more complex aromatic methoxy derivatives.

The dipole moment of quinol dimethyl ether, measured in benzene solution, is about 1.7 Debye units. To account for this high value various explanations had been put forward and the most generally accepted is the one based on the assumption that the methyl groups are rotating about the bonds joining the oxygen atoms to the benzene ring. If it were found by X-ray analysis that such rotation of methyl groups is taking place in the solid state, the above explanation would be confirmed. The compound is very volatile and of

comparatively low density and therefore this possibility had to be investigated.

Various methods have been applied to determine the valency angle of oxygen in dimethyl ether. The most reliable value of this angle is 111 ± 4°, which was obtained by Sutton and Brockway[1] by electron diffraction methods.

In aromatic ethers, however, this angle was determined only from electric dipole moment measurements. Among many workers who investigated this problem were Bergmann, Smyth, Walls, Sutton and Hampson.

In 1934 G.M. Bennett[2,3] criticised the methods used by the above workers and showed that the analysis of the dipole moments of p-substituted anisoles, by which values have been deduced for this angle of 140° or more, is unsound. He demonstrated that the mesomeric moment due to a given group is not constant, but varies from compound to compound. The two groups in para position are connected by a conjugated system of single and double bonds and the presence of one group influences the value of the moment due to the other.

In 1935 L.E. Sutton and G.C. Hampson[4] came to the conclusion that the angle will vary in different aromatic ethers and in many cases will be greater than 110°. They attributed these enlargements of angles to the resonance of the ordinary structure with others in which the oxygen atom forms a double bond with the benzene ring. They expected

that in anisole this type of resonance will cause this angle to approach 125°.

In addition to many approximations and assumptions used in this application a very small error of 0.05 D. in the value of the dipole moment alters the angle to a great extent.

The value of this angle, therefore, cannot be estimated accurately from the dipole moment measurements and a quantitative X-ray analysis, which would give a trustworthy result was really necessary.

It was also important to find whether the bond joining the methyl group to the oxygen atom approached the value of 1.44 A., obtained by L.E. Sutton and L.O. Brockway for dimethyl ether.[1]

The earlier X-ray research work on the aromatic hydrocarbons has shown that in these compounds, to a good approximation, the benzene ring is a regular and planar hexagon.[5] Recently, however, in view of new knowledge and improvement of technique some of these analyses were carried out by three-dimensional methods and it has been shown that slight variations in the carbon-carbon bond lengths are possible. There were even cases of two-dimensional analyses in which a good resolution of many of the atoms allowed differences in bond lengths to be observed[6]. It was therefore

of great interest to find whether the benzene ring of quinol dimethyl ether is a regular and planar hexagon or whether it is distorted.

On undertaking this work it was also expected to establish, if not the accurate positions of hydrogen atoms of the methyl group, at least whether they are fixed or rotating freely about the bond joining the carbon atom of the methyl group to the oxygen atom. It is interesting that in the electron diffraction investigation of the molecular structure of dimethyl ether[1] the possibility of rotation of each of the methyl groups around the corresponding carbon-oxygen bond was taken into account and an allowance for such unrestricted rotations has been made in the calculations of the intensity curves.

Finally it was hoped that this investigation would lead to better understanding of some of the physical properties of this compound.

In conclusion it may be said, that the results justified the undertaking of this work.

RESULTS OF X-RAY ANALYSIS.

Crystal Data.

Quinol dimethyl ether, $C_8O_2H_{10}$; M. 138.08; m.p.56°; d. calc. 1.199, found 1.190; orthorhombic bipyramidal; a = 7.29±0.02, b = 6.30±0.02, c = 16.55±0.03 A. Volume of the unit cell, 760 A^3. Absent spectra: no general halving, (0kl) absent when k odd; (h0l) absent when l odd; (hk0) absent when h odd; (00l) absent when l odd; (0k0) absent when k odd; (h00) absent when h odd. Space group Pbca. (D_{2h}^{15}). Four molecules per unit cell. Molecular symmetry: centre. Total number of electrons per unit cell F(000) = 296. Absorption coefficient for X-rays: λ = 1.54, μ = 8.14 cm.$^{-1}$.

Refractive indices: γ = 1.632, (c); β = 1.610, (b); α = 1.506, (a); negative birefringence 0.126. The letters in brackets denote the crystal axes to which the vibration is parallel.

Quinol dimethyl ether was prepared from hydroquinone. Colourless, rather volatile plates, parallel to the (001) plane were obtained. The crystals were rather soft.[7]

Magnetic rotation measurements were carried out by Perkin[8]. Ultra-violet absorption spectra of quinol dimethyl ether in different solvents were studied[9]. The heat of combustion as determined by F. Stohmann[10] and his co-workers is 1015.076 kg.cals. per gm.mol. Their value for the heat of formation

formation is 81.924 kg. cals.

Dipole moment of quinol dimethyl ether (in benzene) was found to be 1.67 Debye units[11].

Structure Analysis.

The space group Pbca requires eight asymmetric units per unit cell. Since there are only four molecules of quinol dimethyl ether in a unit cell, each molecule must possess a centre of symmetry which coincides with the crystallographic centre of symmetry. The asymmetric unit consists therefore of four carbon, one oxygen and five hydrogen atoms. The diagram of the unit cell showing the position of the asymmetric units and of the symmetry elements is given by International Tables for the Determination of Crystal Structure[12].

In the analysis of the structure by trial it was assumed that the benzene ring was a regular, planar hexagon of radius 1.39 A. The oxygen atoms were assumed to lie on a line passing through the adjacent carbon atoms of the benzene ring and the centre of the molecule. The C_1-O bond length was taken as 1.36 A., as it was assumed that it did not differ very much from the value found by Robertson[13] in resorcinol. The same bond length was obtained by Palin and Powell[14] in the case of the quinol molecule in clathrate

compounds. The bond length between the oxygen and the carbon atom of the methyl group was accepted to be 1.43 Å., being the sum of the covalent single-bond radii of the two atoms as given by Pauling and Huggins[15]. The O-C bond length found in dimethyl ether by the electron diffraction methods agreed very well with this value. The angle C_1OC_m (C_m denotes the carbon atom of the methyl group) was taken as 110°.

The birefringence was found to be negative and not remarkably high (0.126), but since the polarisability of the benzene ring for vibrations perpendicular to its plane is known to be considerably smaller than for vibrations in its plane, the above results definitely indicated that the planes of the molecules were parallel to one another and tended to lie in the (100) plane. The fact that for vibrations along the c axis the R. I. value was the highest indicated that the long molecular axis, i.e., the line passing through two opposite carbons of the benzene ring and the two adjoining oxygen atoms probably lay along the c axis of the crystal.

The (200) plane gave a very strong reflection, (F measured = 96.5), but the reflections of (400) and (800) were very weak. If all the atoms of the molecule were lying on the (100) plane, all these axial reflections would be of approximately equal intensity. These results indicated that only some of the atoms of the molecule were situated in, or very nearly in, the bc crystal plane. Taking the results

of R. I. measurements also into account it seemed very likely that the long axis of the molecule lay nearly parallel to the c axis and that the benzene ring had a tilt not exceeding 45° from the (100) plane.

A wire model of the unit cell was then constructed, the molecules, made on the same scale, were placed at four equivalent points and, keeping in mind that the distance between the carbon atoms of different molecules should not be smaller than 3.6 A., as much information as possible was derived as to the value of the angle of the tilt of the benzene ring from the (100) plane and as to the possible positions of the carbon atom of the methyl group.

The results of this investigation were: -

1. The unit cell dimensions allowed for the long molecular axes to be situated along the c crystal axis.

2. It seemed very likely that the angle between the long molecular axis projected on the bc plane and the c axis (denoted by α) was larger than the angle between the same molecular axis projected on the (010) plane and the c axis (denoted by β). Owing to the proximity of the benzene rings of different molecules the angle β should not be greater than 23°, but was probably not exceeding 5°. The value of α, however, was limited only by the position of the methyl groups.

3. The tilt of the plane of the benzene ring from the (100) plane (the angle of the tilt being denoted by γ),

could have any value not greater than 49°.

4. It was found very improbable that the methyl groups were rotating about the bonds joining the oxygen atoms to the benzene ring, since in such a case the two C_m atoms of the molecules situated at the origin and at $(\frac{1}{2},\frac{1}{2},0)$ would come within 2.5 A. from each other. If the rotation of the methyl groups was considered to be synchronised, the symmetry operations appropriate to the space group Pbca would be contravened. It was also found that for the smaller values of the β angle the larger x coordinate of the C_m atom was likely to be correct.

The possibility of rotation of the methyl groups about the bonds joining the oxygen atoms to the benzene ring was investigated fully and the conclusion was reached that it does not take place. Many trial structures were calculated in which an allowance was made for the rotation, and in no case a reasonable agreement between the calculated and the measured structure factors was obtained. Finally thermochemical measurements were carried out, but again there was no indication of the rotation.

The projection along the a axis on the (100) plane was chosen first, as it was expected that it would give the best resolution. Bearing all the above results in mind, the structure factors for several trial structures were calculated. The angles, $\alpha=15^\circ$, $\beta=3.5^\circ$, and $\gamma=33^\circ$, gave the best

agreement between the measured and the calculated values of F. The F values were very sensitive to the change of coordinates of the carbon atom of the methyl group. After a few trials, however, the y coordinate of 2.152 A. gave sufficiently good general agreement between the F measured and F calculated for the refinement of the atomic positions by two-dimensional Fourier series methods. Four Fourier syntheses were carried out until there were no further changes in the phase constants of any of the observed reflections. A full resolution of all the atoms was obtained and the final coordinates were determined fairly accurately.

At this stage of the work the contribution made by the hydrogen atoms was introduced into the calculation of the structure factors. The bond lengths between the hydrogen and the carbon atoms of the benzene ring were taken as 1.08 A.[16] and the bonds were assumed to be distributed radially, i.e., lying on lines passing through the adjacent carbon atoms and the centre of the benzene ring.

The hydrogen atoms of the methyl group were assumed to be situated tetrahedrally at a distance of 1.09 A.[16] from the carbon atom. ($\angle$ HCH - 109° 28'). In order to find the coordinates of these atoms, the circle on which they were lying was projected on to the (100) plane. An ellipse was therefore obtained, the minor axis of which was calculated assuming the O-C_m bond length as 1.43 A. The hydrogen atoms were then placed on this ellipse in such a way as to agree with

the two-electron contour line of the Fourier pattern.

The introduction of the contribution of the hydrogen atoms lowered the discrepancy between the observed and calculated values of F for most of the planes with sin θ<0.5.

The structure factors were then recalculated using another set of three hydrogen atoms placed on the same ellipse but half way in between the positions accepted previously. These new positions were therefore obtained by rotating the circle with the previous hydrogen atoms through 60°. The discrepancy between the F values became in this case even greater than that obtained without taking the contribution of hydrogen atoms into account. This proved that the final Fourier electron-density diagram does indicate the positions of the hydrogen atoms fairly accurately.

In order to find out whether the methyl group was rotating about the C_m-O bond, the structure factors were calculated in such a way as to account at least roughly for the rotation and the change in discrepancy between the F values was examined. The contribution made by the rotating hydrogen atoms could be calculated by adding up the geometrical structrue factors for all the six positions used in the two sets of previous calculations and then dividing this sum by two. The same result was actually obtained by the much simpler method of finding the average value of F for the corresponding two F calc. values. The agreement between the

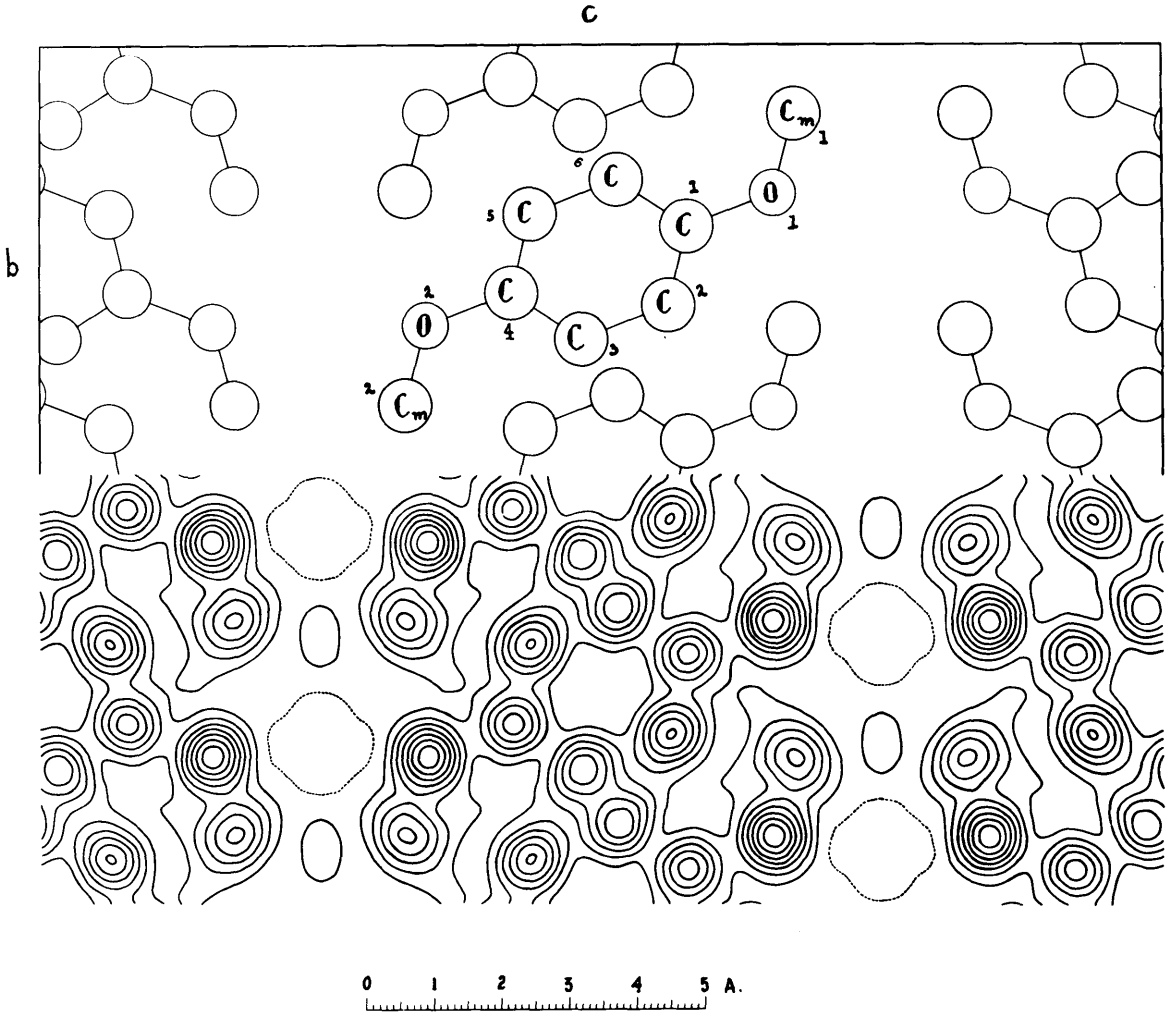
F measured and F calculated was definitely worse than the agreement obtained by placing the hydrogen atoms in fixed positions indicated by the countour map. It appeared therefore that the hydrogen atoms were not rotating.

The introduction of the contribution made by the hydrogen atoms led to the change of the phase constant of the (021) structure factor, and therefore another Fourier synthesis was applied to the (0kl) zone. The F measured for this reflection was too small to alter the coordinates to an appreciable degree, but the shapes of the atoms improved a little.

The final Fourier projection along the a axis is shown in Fig. 1. For this projection the F values of all the observed reflections were taken.

The projection of the benzene ring along the a axis on the (100) plane fulfilled the conditions required by a regular and planar hexagon, as each pair of opposite sides was parallel and one half of the length of the segment through the centre of the ring joining the other two corners. Assuming therefore that the benzene ring was a regular and planar hexagon and taking the bond lengths used in the trial structure it was possible to calculate x coordinates of all the atoms in the asymmetric unit. The structure factors for the (h0l) zone were calculated and reasonably good agreements between the F measured and F calculated values were obtained. The Fourier synthesis was therefore applied. The O_6 atom

Fig. 1.



Projection along the a axis, on the (100) plane. It covers two unit cells. The plane of the molecule is inclined to the projection plane at 33.4°. Each contour line represents a density increment of approximately one electron per A^2, the one-electron line being dotted.

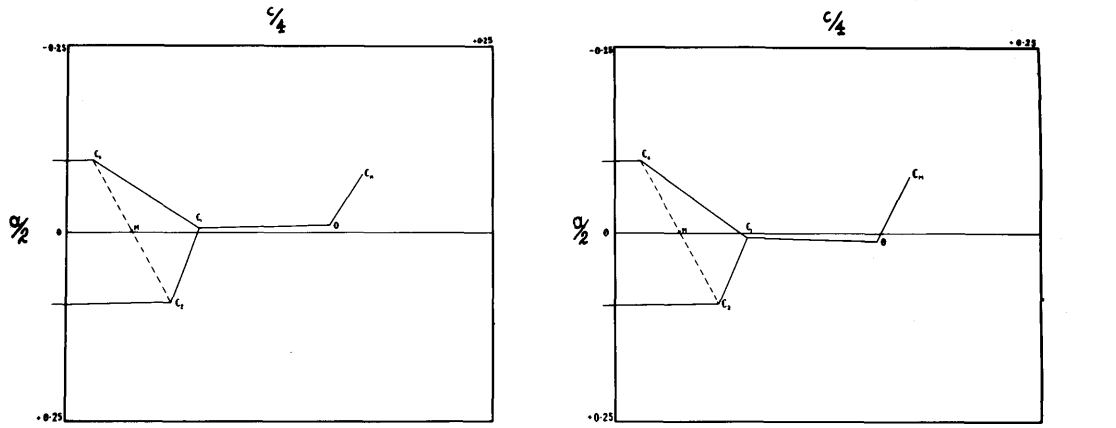
was fully resolved and therefore its x coordinate could be determined fairly accurately, but the refinement of the x coordinates of the remaining four atoms C_1, C_2, O and C_m, was rather difficult owing to overlapping effects. Nevertheless, this first Fourier projection showed that the assumption that the benzene ring was a regular hexagon should be abandoned, as the C_1-C_2 and C_1-C_6 bonds appeared to be considerably longer than the C_2-C_3 bond. It had also indicated that the oxygen and C_1 atoms probably lay on the line passing through the centre of the molecule.

The effect of the contribution of the different resonance structures was considered and it appeared probable that the bonds C_1-C_2 and C_1-C_6 were equal in length. The coordinates of the C_1 and C_2 atoms were therefore taken in such a way as to satisfy this condition and the structure factors were recalculated. The agreements between the measured and calculated structure factors improved considerably and several weak reflections omitted previously could be included in the second Fourier synthesis. The contour map which was obtained did not differ very much from the first one and it was difficult to draw any further conclusions as to the structure of the compound. Several sets of coordinates of the four unresolved atoms, permitted by the contour graph, were therefore taken and the structure factors were calculated for each of them.

If it is assumed that the C_1-C_2 and C_1-C_6 bonds are equal in length and that the line passing through the origin and the C_1 and O atoms bisects the segment joining the C_2 and C_6 atoms, the centres of the benzene ring carbon atoms should be fixed in the projection in such a way as to make the above mentioned line pass through the mid-point of the C_2-C_6 segment.

These assumptions were made in the drawing of Fig.2a, which shows diagrammaticaly the asymmetric unit projected on the ac plane.

Fig. 2.



a b

The atomic centres were fixed using the z coordinates of all the atoms as determined by the projection along the a axis and the information obtained from the second Fourier projection along the b axis. Having fixed the centres of the C_2 and C_6 atoms, the mid-point M of the C_2-C_6 segment was

marked. The C_1 and O atoms were then put on the line drawn through the M point and the origin. The x coordinates of these two atoms were therefore determined by the position of the M point, they agreed reasonably well, however, with the contour lines of the second Fourier projection.

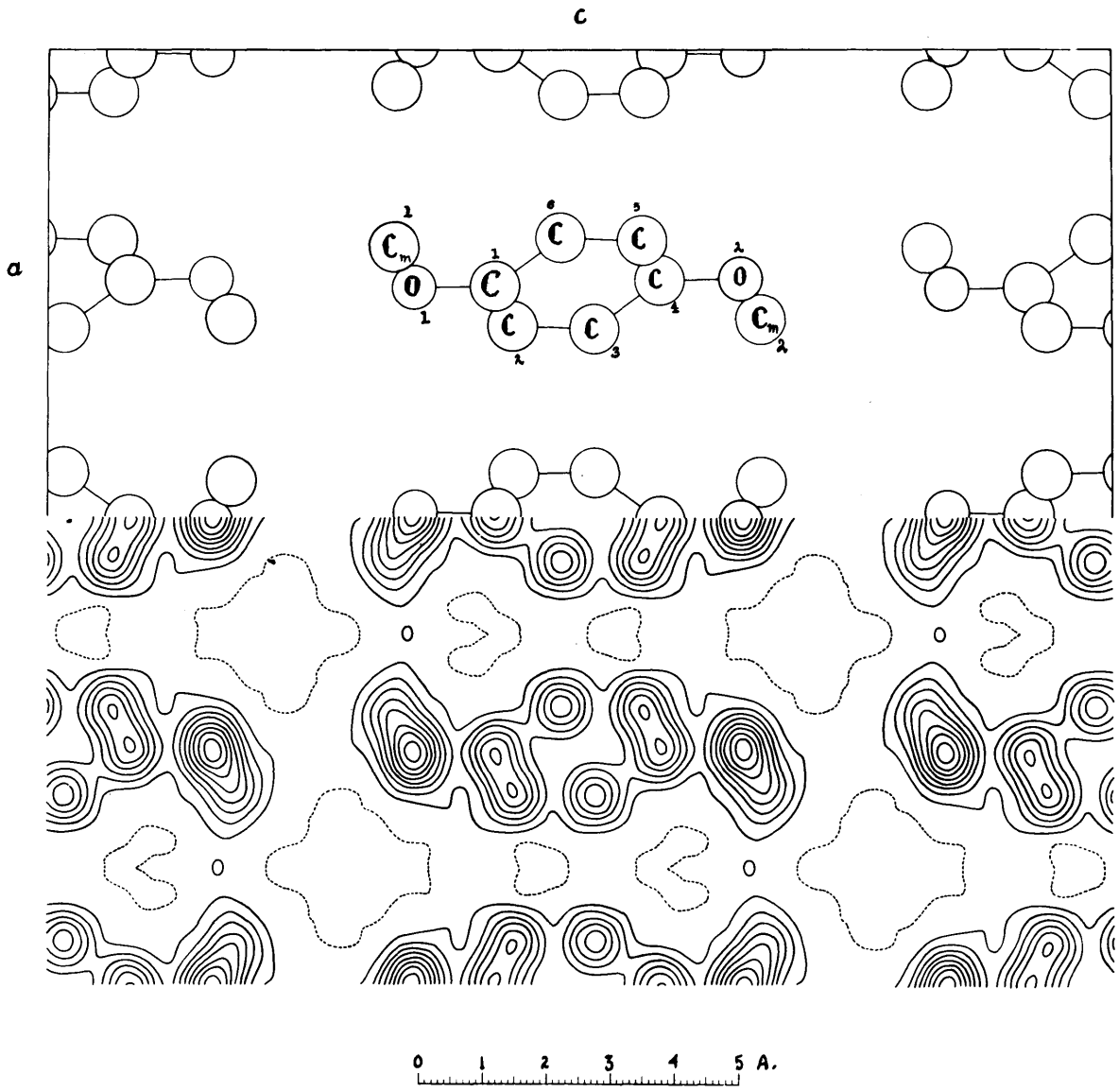
It was found however, that as long as the above condition was satisfied, the discrepancy between the observed and calculated structure factors did not fall below a certain value which was considered to be too high for the application of the final Fourier synthesis. The agreements between the F values for the planes with h even were satisfactory, but for the planes with h odd they were considerably worse. The geometrical structure factors of the latter were calculated by means of the formula $-8\sin 2\pi hx \sin 2\pi lz$ and the F values depended therefore on the sign of the atomic coordinates. It appeared that the results might be improved by changing the sign of the x coordinates of the C_1 and O atoms. The numerical values of these coordinates were very small and only small shifts of their centres were required to place them on the other side of the c axis. The structure factors for positions indicated by Fig. 2b were recalculated for all the planes. A considerable lowering of the discrepancy between the F measured and F calculated resulted (by approximately 7%) and a good general agreement was obtained. More weak reflections could be included in the third Fourier synthesis.

The new contour diagram showed more clearly the positions of the C_1 and O atoms on the same side of the c axis as the C_2 atom. The contributions made by the hydrogen atoms were then included and the coordinates were further refined by the fourth Fourier synthesis.

For all these Fourier series the value of F observed for the (200) plane was 72.5. This value was however, corrected to 96.5 using the data from photographs obtained with smaller crystals and the absolute scale of F measured was adjusted. To see the effect of these changes on the electron density map, the fifth Fourier synthesis was carried out. The positions of the atomic centres were not altered appreciably, but there was a considerable difference in one and two electron contour lines. The effect of introducing the value of F of +90 instead of +71 into the Fourier synthesis was considered by G. A. Jeffrey[17] in his three-dimensional analysis of dibenzyl. The corresponding shift in atomic coordinates was found to be less than 0.003 A. for any atom.

The final Fourier projection along the b axis is shown in Fig. 3. For this final Fourier b axis projection the 2,0,20, 502, 806 and 808 reflections were omitted, as their phase constants were not certain.

Fig. 3.



Projection along the b axis, on the (010) plane, covering two unit cells. Each contour line represents a density increment of approximately one electron per $A.^2$, the one-electron line being dotted.

All the assumptions as to the structure of quinol dimethyl ether were abandoned after the second Fourier projection on the (010) plane was obtained. The shifting of the C_1-O bond to the other side of the c axis gave the distorted benzene ring, but on the other hand, the length of the O-C_m bond increased considerably. The latter was very important, as the value of 1.29 A. for this bond did not seem to be correct.

The projection along the c axis on the (0.01) plane would not give any resolution at all, and therefore the Fourier synthesis was not carried out.

Coordinates, Orientation and Dimensions.

The coordinates of all the atoms with respect to the x, y and z crystallographic axes are given in Table I, the centre of symmetry being taken as the origin. They were measured directly from the electron density maps after abandoning all the assumptions as to the regularity and planarity of the benzene ring, and they gave the best agreement between the observed and calculated values of F. The coordinates of all the other atoms in the unit cell were derived from these by the following operations: -

$$\pm\left[x,y,z;\quad \tfrac{1}{2}+x,\ \tfrac{1}{2}-y,\ -z;\quad -x,\ \tfrac{1}{2}+y,\ \tfrac{1}{2}-z;\quad \tfrac{1}{2}-x,\ -y,\ \tfrac{1}{2}+z;\right]$$

The coordinates of the hydrogen atoms listed were found by

means of ellipses drawn on the (100) and (010) Fourier projections, as described in the Structure Analysis section. The lengths of their minor axes were calculated, taking the $C-C_m$ bond length obtained from the coordinates of these atoms, i.e., 1.35 A. This method was found to be adequate, since the bond lengths between each of the hydrogen atoms and the carbon atom calculated from the final coordinates of these atoms did not deviate by more than 0.015 A. from the accepted value of 1.09 A.

For the final trial structure, the y coordinate of the C_m atom was taken as+2.152 A. It can be seen from Table I that this value did not alter.

Table I.

The coordinates with respect to crystal axes.

Atoms.	x, A.	y, A.	z, A.	$2\pi x/a$.	$2\pi y/b$.	$2\pi z/c$.
C_1	0.040	0.502	1.286	2.0°	28.7°	28.0°
C_2	0.676	-0.672	1.013	33.4	-38.4	22.0
C_6	- 0.712	1.176	0.258	-35.2	67.2	5.6
O	0.076	0.996	2.551	3.8	56.9	55.5
C_m	-0.556	2.152	2.863	-27.5	122.9	62.3
H_2	1.199	-1.192	1.797	59.2	-68.1	39.1
H_6	- 1.263	2.085	0.457	-62.4	119.2	9.9
M_1	-0.120	2.979	2.268	- 5.9	170.2	49.3
M_2	-0.424	2.358	3.921	-20.9	134.8	85.3
M_3	-1.618	2.055	2.644	-79.9	117.4	57.5

M_1, M_2, M_3, are the hydrogen atoms of the methyl group.

The orientation of the molecule was found from the coordinates finally accepted, and again no assumptions of any kind were made. The plane including C_1, C_2, and the centre of the molecule was found to be:-

$$x + 0.604y - 0.267z = 0.$$

It was then found that all other atoms of the molecule lay in, or nearly in this plane, the greatest distance from it being given by the coordinates of C_6 atom(0.06 A.). The oxygen and the C_1 atoms are collinear with the centre of the benzene ring. The molecular axis was therefore chosen passing through these three points and was denoted by L. Second axis, denoted by M, was perpendicular to the L axis at the centre of the molecule and it lay in the plane given by the above equation. The N molecular axis was perpendicular to these and it passed through the centre of the benzene ring. The complete orientation of the molecule is given in the following table, in which χ, ψ, and ω are the angles, which the molecular axes L, M, and N make with the a, b, and c crystallographic axes.

Table II.

Orientation of the molecule in the crystal.

$\chi_L = 88.3^\circ$	$\cos\chi_L = 0.0290$
$\psi_L = 68.7^\circ$	$\cos\psi_L = 0.3635$
$\omega_L = 21.4^\circ$	$\cos\omega_L = 0.9313$
$\chi_M = 56.6^\circ$	$\cos\chi_M = 0.5499$
$\psi_M = 141.6^\circ$	$\cos\psi_M = -0.7836$
$\omega_M = 73.2^\circ$	$\cos\omega_M = 0.2887$
$\chi_N = 33.4^\circ$	$\cos\chi_N = 0.8348$
$\psi_N = 59.8^\circ$	$\cos\psi_N = 0.5036$
$\omega_N = 102.9^\circ$	$\cos\omega_N = -0.2228$

The inclination of the molecular plane to the (100) plane is given by $90^\circ - \chi_M = 33.4^\circ$, which is in very good agreement with the value used in the trial structure analysis.

The coordinates of all the atoms with respect to the molecular axes were then calculated and are collected in Table III.

Table III.

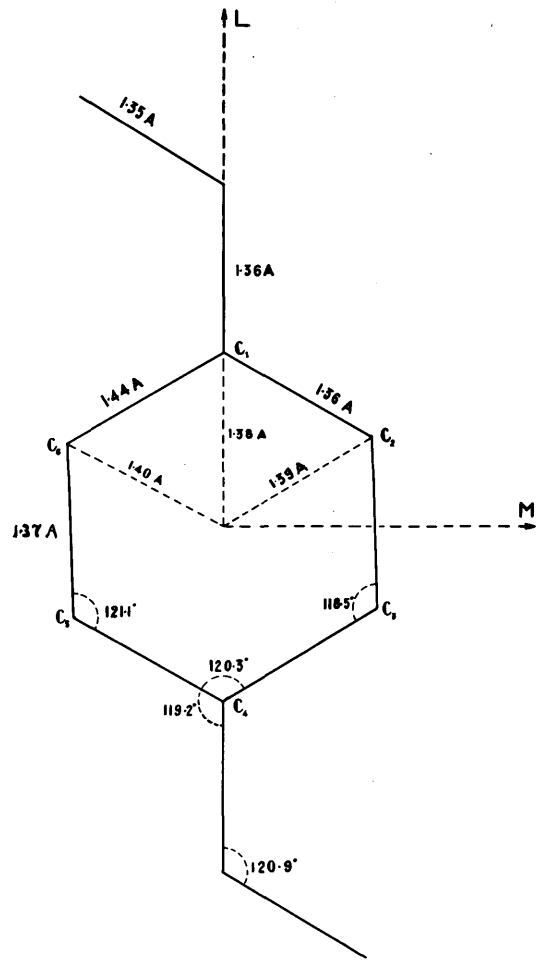
Coordinates with respect to molecular axes.

Atoms	L. A.	M. A.	N. A.
C_1	1.382	0	0
C_2	0.719	1.191	0
C_6	0.647	-1.239	-0.059
O	2.739	-0.002	-0.003
C_m	3.433	-1.165	-0.018

It is interesting that the coordinate of one of the hydrogen atoms of the methyl group, M_g, with respect to the molecular axis N has also a small negative value (-0.039 A.).

The bond lengths and valency angles obtained are shown graphically in Fig. 4.

Fig. 4.



Dimensions of the molecule of quinol dimethyl ether.

Intermolecular Distances.

The closest approach between atoms of different molecules takes place between the molecule at the origin and that reflected at $(\frac{1}{2}, \frac{1}{2}, 0)$. If the former molecule is denoted by a, and the latter by b, the following distances are observed:

$$C_1^a - C_2^b = 3.54 \text{ A.}$$

$$C_2^a - C_2^b = 3.90 \text{ A.}$$

$$C_6^a - C_2^b = 3.98 \text{ A.}$$

$$C_3^a - C_3^b = 3.86 \text{ A.}$$

$$O_2^a - C_{m_1}^b = 3.75 \text{ A.}$$

Another molecule at $(\frac{1}{2}, 0, \frac{1}{2})$ was taken and denoted by c, and it was found that there was no close approach between this molecule and the standard a, all distances being greater than 4.0 A.

There remains only one short distance, which should be mentioned, i.e., that between $O_1^b - C_{m_1}^c$, which gave the value of 3.52 A. This is the smallest intermolecular distance observed and it agrees well with the sum of the van der Waals radii of the oxygen atom and the methyl group, which amounts to 3.4 A.[18]

The distances between the carbon atoms of the methyl

groups were found to be:-

$$C^{a}_{m_2} - C^{b}_{m_2} = 4.04 \text{ A.}$$

$$C^{b}_{m_1} - C^{c}_{m_1} = 4.20 \text{ A.}$$

They are of expected magnitude, since the van der Waals radius of the methyl group is 2.0 A.

All the above results showed that there was no intermolecular distance smaller than allowed by the van der Waals forces.

Quinol dimethyl ether crystallises in the form of plates parallel to the (001) plane. This can be explained by the fact that the approach between the molecules, the centres of which are of the same z coordinate, is not nearly so close as in any other direction. This can be seen clearly in Fig. 1. and Fig. 3.

EXPERIMENTAL.

Preparation.

Quinol dimethyl ether was prepared from hydroquinone by methylation with dimethyl sulphate in presence of sodium hydroxide solution. The method used was that described by Vermeulen.[19]

The recrystallisation from dilute ethyl alcohol gave thin, colourless, volatile plates of m.p. 55° - 56°. Several different organic solvents have been used for recrystallisation, but they all gave the same form of crystals. The best samples for X-ray analysis were obtained by using 60° - 80° petroleum ether. By slowing down the rate of crystallisation as much as possible, by means of a Dewar flask, thick plates (up to 1.2 mm. thickness) were obtained, which were then cut to a suitable size.

These plates were invariably parallel to the (001) plane. To facilitate the setting of crystals all care was taken to cut their sides parallel to their crystallographic axes. This was difficult owing to softness of the crystals and the fact that the directions of extinction had to be examined many times during the cutting process.

Measurement of Refractive Indices.

The indicatrix for an orthorhombic crystal is a triaxial ellipsoid, the axes of which correspond with the three crystallographic axes, therefore refractive indices of quinol dimethyl ether determined along the extinction directions gave the values along the crystal axes. The method of central illumination called the"Becke method" was used.[20]

Quinol dimethyl ether was found to be soluble in most of the organic liquids commonly used for R. I. estimations. This difficulty was overcome by preparing potassium mercuric iodide solution by the method described by Wherry[21]. This solution of R. I. approximately 1.65 was subsequently diluted with different quantities of glycerol to give several mixtures of lower indices. The refractive index of every medium selected was measured directly before use by means of an Abbé refractometer.

In order to obtain any information as to the structure of quinol dimethyl ether it was necessary to identify each crystal axis along which the R.I. was measured. As soon as the R. I. along one of the extinction directions was determined the crystal was cleaned of the medium, mounted, set about that axis and X-ray photograph was taken. This procedure was used for identification of both the a and the b axes.

The largest R.I. (γ=1.632) was found to be along the

c crystal axis and the smallest (α-1.506) along the a axis. The R.I. along the b axis, β, is 1.610.

X-ray Measurements.

The crystals were rather volatile and those of 0.5mm. thickness did not last longer than a day at ordinary room temperature. In order to protect them small gelatine capsules were used to surround the mounted crystals. Owing to a considerable scattering of X-rays, however, they produced darkening on the X-ray photographs, which affected the intensity measurements of all the reflections of large spacing. This method was therefore abandoned when photographs used for intensity estimations were taken. In order to obtain an exposure of several hours on a moving film photograph using an unprotected crystal at room temperature, it was necessary to cut it and set it within a few hours, otherwise it would have volatilised.

All the X-ray work was carried out with Cu-K_α radiation (λ-1.54). Rotation and moving film photographs about the a, b, and c crystal axes and oscillation photographs about the a axis were taken, the crystals in all cases being completely immersed in a uniform X-ray beam.

The crystals were cut, so that they approached the shape of a cube as nearly as possible.

For the first moving-film photographs about the a, b, and c crystal axes the specimens used were as small as possible, so small in fact that at the end of each four hour exposure they could scarcely be detected. Using such small crystals, however, only the moving-film photograph about the a axis was successful showing 60% of all possible reflections, this percentage being considerably lower for the other two zones. In order to obtain weak reflections of the (h0l) and (hk0) zones moving-film photographs were taken using larger crystals.

The linear absorption coefficient for quinol dimethyl ether is large (8.14 $cm.^{-1}$) and therefore the length of the path of X-ray through the crystal should not exceed 0.246 cm., if the photographs were to be used for intensity measurements.[22] The crystals used for moving film photographs about the b and c axes were, at the beginning of the exposures, cubes of sides not greater than 1.2 mm. and were therefore well within the above limit. They were, however, considered to be too large for the absorption corrections to be neglected; these were therefore applied in both cases. The absroption correction factors for the (h0l) zone varied from 1.51 to 1.71 and for the (hk0) zone from 1.52 to 1.82. The absorption corrections for the (hk0) zone had a slightly wider range due to the fact that the sides of the crystal were 0.1 mm. different in length. In both cases the crystals were measured before and after the

exposure and their average dimensions were taken for the calculation of absorption corrections.

The percentage of reflections present for all possible reflections was 86% for the (h0l) zone and 88% for the (hk0) zone.

All the intensities were estimated visually using Robertson's multiple film technique[23]. The range of observed intensities varied considerably for different moving-film photographs. The widest was for the (hk0) zone, which gave the intensity values ranging from 27500 to 1.

The formulae and correction factors used for mosaic crystals were employed. The correction factor for the unpolarised radiation $\frac{\sin 2\theta}{1+\cos^2 2\theta}$ was applied.

For the calculation of F observed for the (h0l) and (hk0) zones the intensities of the photographs of the larger crystals were taken. It was found however, that the intensities of all very strong reflections had considerably lower values than those estimated from photographs obtained using small crystals. The lower intensity values gave greater discrepancy between F observed and F calculated from the atomic positions. The higher F values obtained by using small specimens were considered to be more correct and they were therefore adopted for the following reflections:- 200, 104, 108, 204, 2,0,12, 304, 3,0,12, and 404 for the (h0l) zone, and 020,

040, 210, and 250 for the (hk0) zone. These corrections were made after careful correlation by means of all the weaker reflections.

The absolute scale of F was not determined directly, but was obtained by correlation with the values finally calculated from the atomic positions. The results are collected in Table V under 'F, meas.'.

Structure Factors.

A complete list of structure factors is given in a convenient form in "Structure Factor Tables" by K.Lonsdale.[24]

The following simplified formulae were used:-

For the (0kl) zone: $A = +8\cos 2\pi ky \cos 2\pi lz$; when l is even.

$A = -8\sin 2\pi ky \sin 2\pi lz$; when l is odd.

For the (h0l) zone: $A = +8\cos 2\pi hx \cos 2\pi lz$; when h is even.

$A = -8\sin 2\pi hx \sin 2\pi lz$; when h is odd.

For the (hk0) zone: $A = +8\cos 2\pi hx \cos 2\pi ky$; when k is even.

$A = -8\sin 2\pi hx \sin 2\pi ky$; when k is odd.

$B = 0$ in all cases.

The contoured graphs[25] were employed for the calculation of structure factors of the axial and several general reflections. They were not used, however, in the calculation of the final structure factors, which are listed in Table V. under 'F, calc.'.

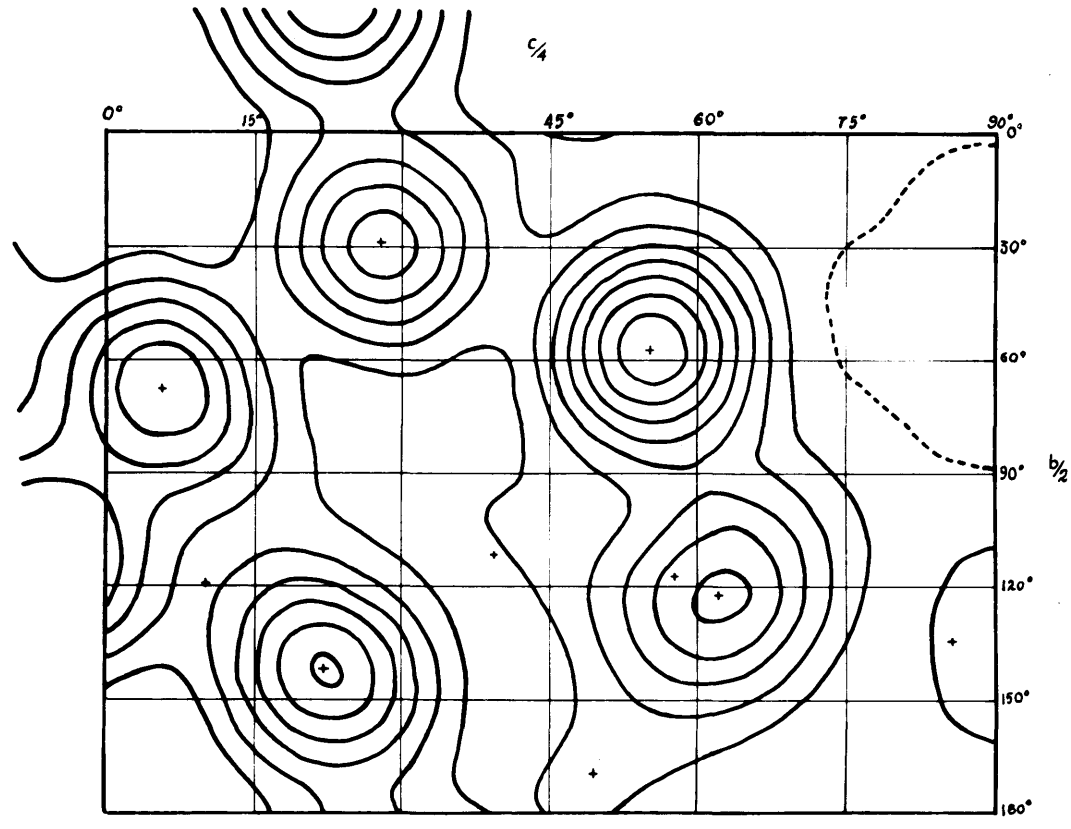
Fourier Analysis.

Five successive Fourier syntheses were carried out for each of the (0kl) and (h0l) zones. The series was set up according to the usual formulae[26] using the measured values of F with the phase constants determined from the trial structures.

For the first two Fourier projections along the a axis on the (100) plane and along the b axis on the (010) plane, Beevers and Lipson[27] strips were used, and the summations were carried out at 450 points on the asymmetric unit, the three crystal axes being divided into 60 parts in each case. For the remaining Fourier syntheses the three figure methods[28] were used. It was then possible to divide the c axis into 120 intervals of 0.138 A., since $\frac{1}{60}^{th}$ part of the c axis, 0.276A., was rather large for accurate graphical interpolation. The a and b axes were, as previously, divided into 60 parts giving intervals of 0.122 A. and 0.105 A. respectively. The summations were carried out at 900 points on the asymmetric unit. The contour lines were plotted on a scale of 5 cm. to 1 A. by graphical interpolation from the summation totals. The sections of both the rows and the columns were made.

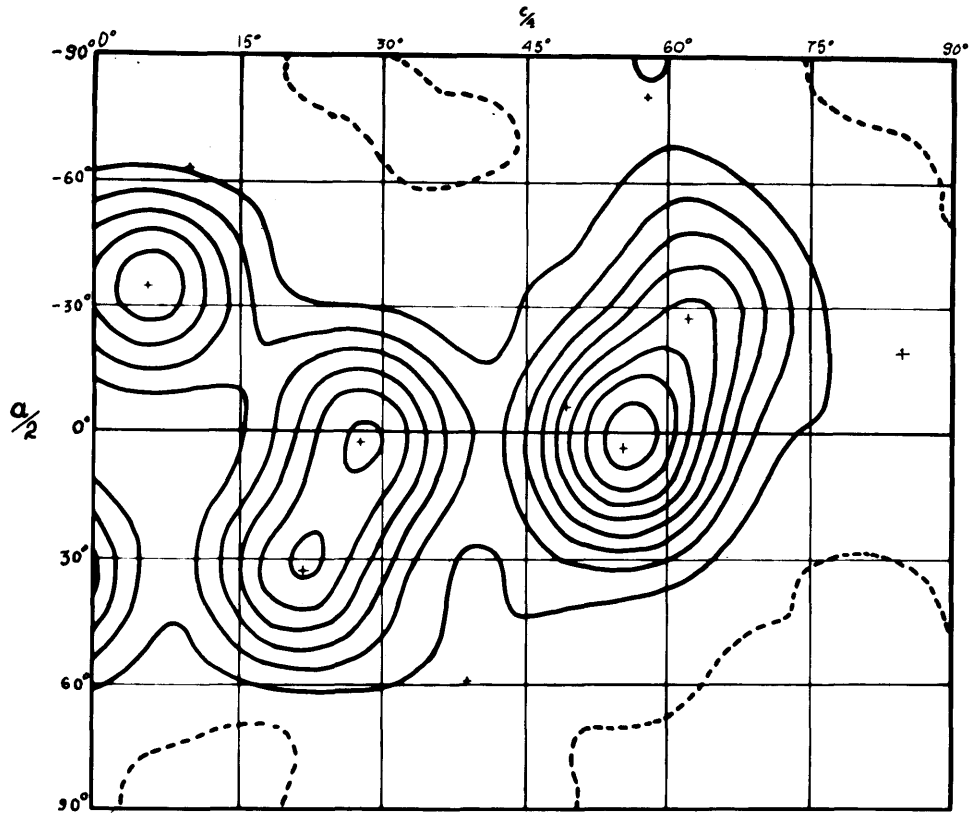
The final contour maps of the asymmetric unit are shown in Figures 5 and 6, and in these diagrams the positions finally assigned to the atomic centres are marked by small crosses.

Fig. 5.



Coordinates assigned to the atoms in the bc projection of the asymmetric unit of quinol dimethyl ether. The positions of the hydrogen atoms are also shown.

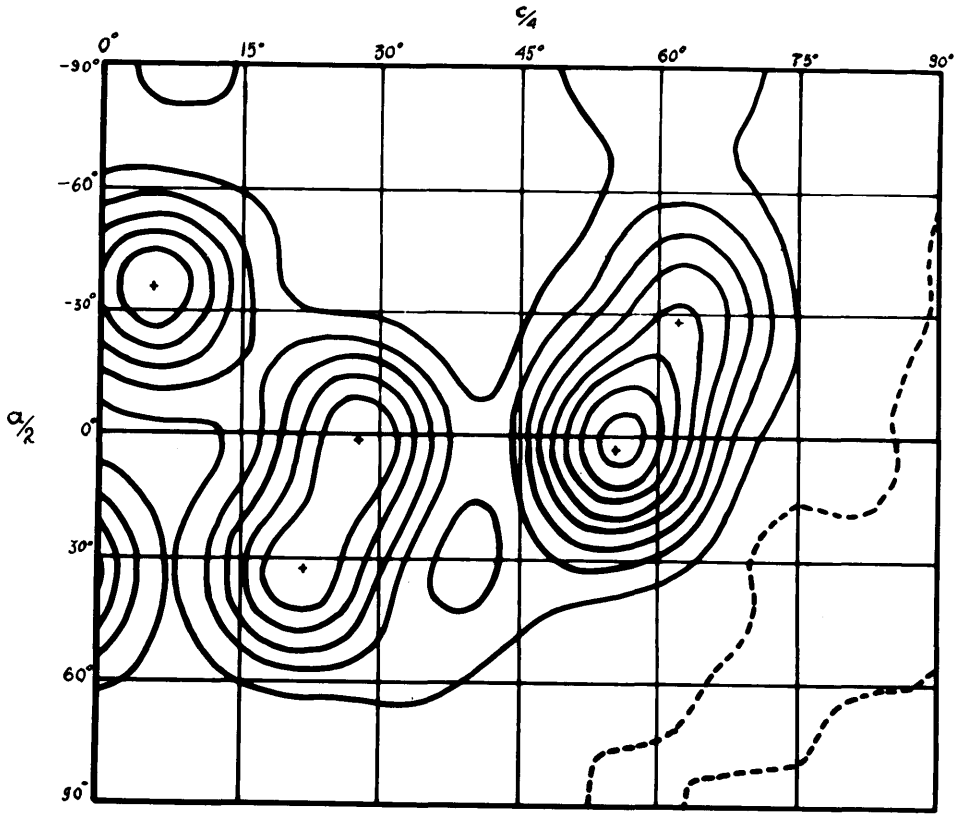
Fig. 6.



The asymmetric unit projected along the b axis on the (010)plane.

On close examination of Fig. 6, it appeared that to make some of the atomic centres agree better with the electron contour lines, slight shifts of these atoms should be made. The final coordinates which are marked in Fig. 6 were actually determined from the previous Fourier projection which is shown in Fig. 7.

Fig. 7.



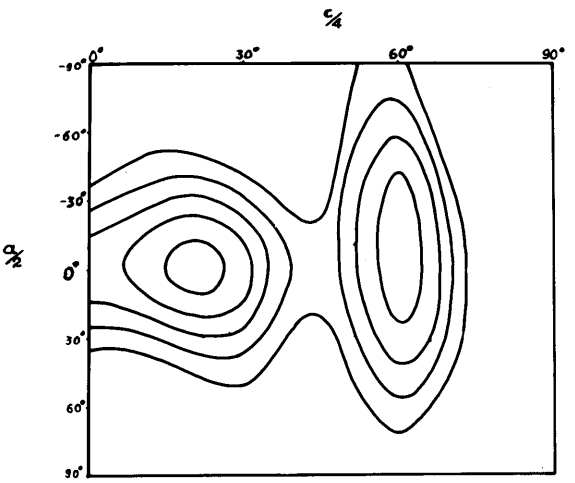
The b axis projection carried out using the value of +72.5 of F for the (200) plane.

The Fourier projection shown in Fig. 7 differs from the final one in Fig. 6, in that for the latter the value of F for the (200) plane was corrected from +72.5 to +96.5 and the corresponding readjustment of the scale of 'F meas.' was made. The changes in the positions of the atomic centres were very small, nevertheless, they would have been taken into account,

had it not been extremely difficult to fix them in accordance with the information obtained from the a axis projection. For example, the final b axis projection indicated that the C_2 atom should be shifted in such a way as to decrease its z coordinate. The a axis contour map (Fig. 5) shows however, that the z coordinate of this atom should be increased. Since in the projection along the a axis all the atoms were fully resolved, more value was attached to the information derived from it, and in the end it was decided not to change the coordinates determined from the b axis projection shown in Fig.7.

Before all the above mentioned Fourier syntheses were carried out, an electron density map for the (h0l) zone was obtained. It is shown in Fig. 8, and it should be compared with the final contour map for the same zone given in Fig. 6.

Fig. 8.



Projection along the b axis showing the asymmetric unit of quinol dimethyl ether.

Fig. 6 shows two elliptical contours due to the proximity of two carbon atoms of the benzene ring and of the oxygen and carbon atom of the methyl group. The first Fourier projection, however, did not show any resolution of the benzene ring atoms and the ellipse given by the O and C_m atoms had a long major axis. These unsatisfactory results were due to the fact that only a few structure factors of h odd were included for the Fourier synthesis and about half of these had wrong phase constants assigned to them. The structure factors concerned were calculated by means of the formula $-8\sin 2\pi hx \sin 2\pi lz$, and if half of the F values included in the synthesis were used with wrong phase constants, the contour map should have shown certain characteristics of the asymmetric unit and also of its mirror image.

This first Fourier map was important as it led to a faulty conclusion which had hindered the work for some time. The presence of the ellipse of long major axis suggested that the methyl group was rotating, the axis of rotation being the line joining the oxygen atom and the adjoining carbon atom of the benzene ring. Structure factors were then calculated to account for the rotation. This was done by calculating the geometrical structure factors for four different positions of the carbon atom of the methyl group, (taken at the end points of the major and minor axes of the ellipse obtained by assuming bond lengths and orientation of the molecule), and then

averaging them. These calculations did not give any improvement in the agreement between F measured and F calculated.

Before the concept of the rotation of the methyl group was abandoned it was considered necessary to apply thermochemical measurements. If the methyl group was rotating at room temperature, it was likely that this would cease at a lower temperature. The change of energy of the molecule which would therefore result would be indicated by the time-temperature curve. The substance was cooled gradually in a Dewar flask by means of acetone with solid CO_2 down to $-60^{\circ}C$, the temperature being read off every 30 seconds. A n-pentane thermometer was used and precautions to exclude moisture were taken. The time-temperature curves were plotted, but they did not show any transition periods. Liquid oxygen was then used to cool quinol dimethyl ether to $-200^{\circ}C$, but again the rotation of the methyl group was not indicated.

Atomic Scattering Curves.

Originally the scattering curve given for hydrocarbons by J. M. Robertson[29] was used for all the atoms in the molecule, weighting the atomic scattering factor of oxygen atoms in the ratio of 8 to 6 with respect to the carbon atoms. This curve had been obtained from the X-ray measurements performed on graphite and hexamethylbenzene and had been corrected, extended and calibrated with the anthracene results. It was found, however, that the observed values of F were consistently lower than the calculated F values for small spacing planes, while those of large spacing tended to be slightly higher. The Robertson's curve was therefore slightly modified and the f-values used are as follows:-

(max^{m}. $f = 1$), -

$\sin\theta$ / $\lambda = 1.54$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
f	.740	.574	.446	.338	.245	.176	.122	.079	.047

...1.

On comparison with Robertson's values it can be seen that they are almost identical for planes of $\sin\theta < 0.6$, the main difference between the two curves lying in the fact that the curve used for quinol dimethyl ether gives lower values of the atomic scattering factor for small spacing planes. This alteration seemed to be justified, since 1:4 dimethoxybenzene is a very volatile compound and there was little doubt that the tempe-

rature factor was larger than in the case of compounds from which Robertson's values of atomic scattering factors had been derived.

The structure factors were recalculated weighting the oxygen atoms in the ratio of 9 to 6 with respect to the carbon atoms, but there was no improvement in the agreement with F observed. This method was therefore abandoned.

It was found, however, that the discrepancy between F observed and those calculated would decrease considerably if a different scattering curve was used for the carbon atom of the methyl group (C_m). The effect of several curves on the values of calculated F's was studied and the curve which gave the best results was used, and is given below:- (max. $f_{C_m} = 1$). -

$\sin\theta$ / $\lambda = 1.54$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
f_{C_m}	.870	.606	.430	.307	.221	.156	.105	.063	.032

...2.

This curve crossed Robertson's curve at $\sin\theta = 0.255$. It gave slightly higher f values for planes of $\sin\theta < 0.255$, but considerably lower values for small spacing planes. The deviation of this curve from Robertson's is more marked than in the case of the curve no. 1., but the deviation is in the same direction. The fact that the methyl group is more mobile than the rest of the molecule was also indicated by the shape of

the atom C_m on the X-ray electron density map.

The curve No. 1 was therefore used only for the oxygen atoms and for the carbon atoms of the benzene ring.

The third scattering curve was used for the hydrogen atoms. The curve No. 1 used for these atoms was found unsatisfactory, as, although a better agreement between the values of $F_{observed}$ and F calculated resulted for most of the large spacing planes, the agreement became worse for all the planes of $\sin\theta > 0.7$. This indicated that hydrogen atoms should not contribute at all to the values of the structure factors of small spacing planes. The scattering curve used by Morrison[30] for the hydrogen atoms of sebacic acid was therefore adopted. The following values were used for its plotting:- (f_H max. = 1).

$\sin\theta$ λ=1.54	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7 ....3.
f_H	1	.83	.58	.36	.20	.087	.029	0

The discrepancy between F measured and $F_{calc.}$ was calculated by means of the formula:-

$$\frac{\sum(|F \text{ meas.}| - |F \text{ calc.}|)}{\sum|F \text{ meas.}|}$$

The discrepancies found were: 12.2% for the (0kl)

zone, 11.5% for the (h0l) zone, 9.1% for the (hk0) zone, and 13.0% for all the reflections.

These results included the discrepancies for all the unobserved reflections. This was done by including in the numerator of the above expression the values obtained from subtracting F measured from F calculated, whenever the value of the latter was greater than the maximum possible value of F observed.

The F values of all these unobserved reflections were omitted for the calculation of the total sum of F meas. and F calculated, and therefore did not affect the value of the denominator of the above formula. (ΣF calc. = 1185.5; ΣF meas. = 1192.5). If the F values of all the unobserved reflections were not taken into account, the discrepancy decreased by approximately 0.5% for the (0kl) and (h0l) zones, the difference being negligible for the (hk0) zone. The total discrepancy in this case was 12.4%.

All these values were obtained after the introduction of the contribution made by the hydrogen atoms, which had lowered the discrepancy for all the reflections by 4%. The lowering of discrepancy was therefore not so marked as in the case of sebacic acid[30], which gave a lowering of discrepancy by 5.4% for the reflections of sin $\theta < 0.4$. This result was, however, expected, since the percentage of hydrogen atoms for all atoms in the molecule is lower in the case of quinol

dimethyl ether.

The introduction of the contribution made by the hydrogen atoms affected the values of F of large spacing planes to a remarkable degree, and in the case of the (021) plane a change of phase constant was obtained.

These results indicate that if the contribution made by the hydrogen atoms is not taken into account, it is advisable to omit the values of F of very weak, large spacing planes for the Fourier synthesis, as their phase constants are doubtful in spite of the good agreement which might be found between the corresponding F calculated and F measured values.

A small list of some of the planes the F values of which were affected most by the introduction of the hydrogen atoms' contribution is given in Table IV.

The general agreement between F values was found to be much more satisfactory after accounting for contributions made by the hydrogen atoms and the mathematical correction advocated by Booth[31] were not carried out.

Table IV.

hkl	F meas.	F calc.	
		A	B
020	27.0	-25.0	-21.5
002	34.0	37.5	40.0
004	25.0	-26.5	-22.5
008	24.0	-23.0	-27.5
021	2.5	2.5	- 7.0
022	3.0	3.0	5.0
029	10.0	-12.5	-14.0
102	3.5	4.5	1.5
104	23.0	-23.0	-20.0
106	6.5	4.5	1.0
108	13.5	14.0	10.0
202	7.5	5.0	9.5
206	13.0	11.0	13.5
208	15.0	-15.0	-16.5
210	54.5	57.0	48.0
220	2.5	- 2.0	- 7.5
410	15.0	18.5	20.5

A = the contribution made by the hydrogen atoms being included.

B = F calculated before this contribution was taken into account

Table V.

Measured and calculated values of the structure factor.

hkl	sin θ (λ=1.54)	F,meas.	F,calc.	hkl	sin θ (λ=1.54)	F,meas.	F,calc.
200	0.211	96.5	96.5	024	0.308	8.0	- 7.0
400	0.422	8.5	9.0	025	0.338	16.5	12.5
600	0.633	1.5	- 3.0	026	0.371	36.5	-37.0
800	0.845	5.5	5.0	027	0.407	3.0	6.5
020	0.245	27.0	-25.0	028	0.445	10.0	-12.5
040	0.489	36.5	-35.5	029	0.485	10.0	-12.5
060	0.733	4.0	6.0	0210	0.526	< 2.0	0.5
080	0.977	2.5	- 2.0	0211	0.567	4.0	- 1.5
002	0.093	34.0	37.5	0212	0.610	< 2.5	- 3.5
004	0.186	25.0	-26.5	0213	0.652	6.0	- 6.0
006	0.279	33.0	31.5	0214	0.696	5.5	3.0
008	0.372	24.0	-23.0	0215	0.739	16.0	-17.5
0010	0.465	22.0	-20.5	0216	0.783	3.5	3.0
0012	0.558	26.5	27.0	0217	0.828	< 2.5	- 2.0
0014	0.651	11.5	11.5	0218	0.872	< 2.0	- 1.0
0016	0.744	1.5	- 1.0	0219	0.917	< 2.0	2.5
0018	0.837	2.0	2.0	0220	0.962	< 1.5	- 0.5
0020	0.930	2.5	- 1.0	041	0.491	< 2.0	0
				042	0.498	2.0	- 2.5
021	0.249	2.5	2.5	043	0.508	3.0	0.5
022	0.262	3.0	3.0	044	0.523	10.0	9.5
023	0.282	11.5	-11.0	045	0.541	3.0	- 2.0

Table V. - continued.

hkl	sin θ (λ=1.54)	F,meas.	F,calc.	hkl	sin θ (λ=1.54)	F,meas.	F,calc.
046	0.563	4.0	- 3.5	0611	0.894	< 2.0	0
047	0.587	7.0	8.0	0612	0.922	< 2.0	1.5
048	0.614	11.0	12.5	0613	0.950	< 1.5	0
049	0.643	15.0	17.0	0614	0.980	< 1.0	- 1.5
0410	0.675	10.5	10.0	081	0.978	< 1.0	- 1.0
0411	0.708	< 2.5	3.5	082	0.982	< 1.0	- 1.0
0412	0.742	8.5	- 6.5	083	0.987	< 1.0	- 0.5
0413	0.778	< 2.5	- 0.5	084	0.995	< 1.0	- 1.0
0414	0.814	3.5	- 3.5				
0415	0.852	4.5	3.5	102	0.141	3.5	4.5
0416	0.890	< 2.0	0	104	0.215	23.0	-23.0
0417	0.930	< 1.5	- 0.5	106	0.300	6.5	4.5
0418	0.969	< 1.5	- 1.0	108	0.390	13.5	14.0
061	0.735	< 2.5	- 1.5	1010	0.479	5.5	6.5
062	0.739	4.5	- 6.0	1012	0.570	12.5	12.5
063	0.746	2.5	- 4.5	1014	0.662	7.0	7.5
064	0.757	< 2.5	- 1.0	1016	0.752	1.0	1.0
065	0.769	5.5	- 6.0	1018	0.844	2.5	1.5
066	0.785	14.5	15.5	1020	0.936	< 0.5	0
067	0.802	3.5	- 3.0	202	0.231	7.5	5.0
068	0.822	6.5	5.0	204	0.282	26.5	-26.5
069	0.845	< 2.5	0.5	206	0.351	13.0	11.0
0610	0.868	< 2.0	- 1.5	208	0.429	15.0	-15.0

Table V. continued.

hkl	sin θ (λ=1.54)	F,meas.	F,calc.	hkl	sin θ (λ=1.54)	F,meas.	F,calc.
2010	0.514	15.0	-15.0	4016	0.858	7.0	- 5.5
2012	0.599	18.0	18.5	4018	0.938	3.5	- 2.0
2014	0.687	10.0	9.0	502	0.536	2.0	- 1.0
2016	0.774	4.0	- 3.5	504	0.560	2.0	- 6.5
2018	0.864	< 0.5	0	506	0.597	1.5	1.0
2020	0.954	1.5	- 0.5	508	0.646	1.0	1.0
302	0.330	4.0	- 2.0	5010	0.704	< 1.0	- 0.5
304	0.368	20.0	-24.5	5012	0.769	4.0	4.0
306	0.423	3.5	2.0	5014	0.838	< 0.5	0
308	0.489	7.0	11.5	5016	0.913	< 0.5	- 1.5
3010	0.564	7.5	7.0	5018	0.990	< 0.5	0.5
3012	0.643	18.0	18.0	602	0.639	7.5	- 6.5
3014	0.727	8.5	9.5	604	0.659	11.5	-12.5
3016	0.809	1.0	0.5	606	0.693	4.5	- 4.5
3018	0.895	3.5	2.5	608	0.735	< 1.0	2.0
3020	0.982	< 0.5	0	6010	0.786	1.5	- 3.0
402	0.433	14.0	-16.0	6012	0.845	3.5	2.0
404	0.461	24.0	-27.0	6014	0.908	3.0	3.0
406	0.506	2.0	- 2.5	6016	0.977	4.0	- 3.0
408	0.563	2.5	- 2.0	702	0.745	1.5	- 2.5
4010	0.629	7.0	- 7.5	704	0.762	4.0	3.5
4012	0.702	8.0	7.0	706	0.790	2.0	1.0
4014	0.778	6.0	5.0	708	0.828	3.5	- 3.5

Table V. - continued.

hkl	sin θ (λ=1.54)	F,meas.	F,calc.
7010	0.873	2.5	- 2.0
7012	0.926	4.5	- 2.0
7014	0.984	4.0	- 3.0
802	0.850	1.5	2.0
804	0.865	2.5	- 2.5
806	0.889	2.0	- 0.5
808	0.923	2.0	0
8010	0.964	< 0.5	- 1.0
902	0.955	< 0.5	- 1.5
904	0.968	2.0	2.0
906	0.991	< 0.5	0.5
210	0.244	54.5	57.0
220	0.323	2.5	- 2.0
230	0.423	9.5	8.0
240	0.532	21.0	-21.0
250	0.646	8.5	- 8.5
260	0.763	1.5	3.0
270	0.881	< 1.0	0.5
280	0.999	< 0.5	- 1.0
410	0.440	15.0	18.5
420	0.488	5.5	7.0
430	0.559	5.0	4.0
440	0.646	4.0	- 3.0
450	0.743	2.5	- 4.5
460	0.846	3.0	- 0.5
470	0.954	< 1.0	0
610	0.645	6.5	- 7.0
620	0.679	5.0	5.0
630	0.732	1.5	- 2.0
640	0.800	< 1.5	0.5
650	0.880	1.5	1.0
660	0.969	2.5	- 0.5
810	0.854	8.0	- 7.5
820	0.879	1.5	0.5
830	0.921	2.0	- 2.0
840	0.975	2.0	- 1.5

DISCUSSION OF RESULTS.

The most striking feature of the results of the X-ray analysis of quinol dimethyl ether is that the C-C bonds of the benzene ring vary considerably in length.

These observations are supported by the results of the X-ray analysis of anthracene[32] and graphite[33], since in both of these substances the bonds in the benzene rings were found to vary from 1.36 A. to 1.44 A. Considerable differences in length of these bonds were also obtained in the case of naphthalene[34] and para-nitraniline[35].

Before any attempt is made to explain the bond length variations in quinol dimethyl ether, it is necessary to decide whether these are experimentally significant.

J. M. Robertson and J. G. White[36] studied experimentally the accuracy obtained by two-dimensional X-ray analysis and Fourier series methods and they reached the conclusion that the convergence of the Fourier series is of much greater importance than the extreme accuracy of intensity measurements. They found that for a convergent series with carefully determined intensities the maximum error in bond lengths in a complex structure, should not exceed 0.03 A.

In the case of quinol dimethyl ether both of these conditions were satisfied and therefore it can be assumed that the accuracy of the bond lengths lies within ±0.02 A. or ±0.03A.

In the "Experimental" section of this work a full account may be found of all precautions taken to ensure accurate intensity measurements. The series were fairly complete, since 60% of all possible reflections were used for the final projection along the a axis and 81% for the projection along the b axis.

The coordinates of the atoms in the asymmetric unit were derived by the method of direct adjustment to give the best agreement between structure factors calculated from observed intensities and those calculated from trial structures. The satisfactory agreements were obtained and they are supporting the results of this work.

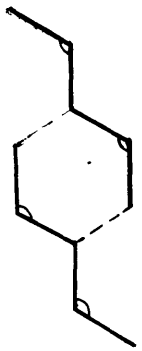
Further, since all the atoms of the asymmetric unit were fully resolved on the projection along the a axis the accuracy of the analysis was increased.

The bonds C_m-O, O-C_1, C_1-C_2, and C_2-C_3, were found to vary in length by a small amount, approximately equal in each case. The following results were obtained: -

Bond.	Length.
C_m-O	1.354 A.
O -C_1	1.358 A.
C_1-C_2	1.362 A.
C_2-C_3	1.368 A.

No importance can be attached to this gradual increase in the bond lengths along the chain C_m-O-C_1-C_2-C_3, however, until it could be confirmed by more reliable results from a three-

dimensional Fourier analysis of this compound. It can only be said, that these four bonds tend towards equality in length and that the molecule appears to consist of two of these "chains" joined by the two longer C_1-C_6 and C_3-C_4 bonds.



The lengths of the benzene ring carbon-carbon bonds give an average value of 1.39 A., and the same is also true for the distances between the individual carbon atoms of the benzene ring and the centre of the molecule.

The valency angles are probably accurate to $\pm 1.5^{\circ}$, It may be significant however, that the two angles $< C_M O C_1$ and $< C_1 C_2 C_3$, which are connected with the "chain" of four approximately equal bonds (they are shown in the above drawing) were found to be almost identical, (120.9° and 121.1° respectively), whereas the angle $< C_1 C_6 C_5$ is appreciably smaller. The average value of valency angles of the benzene ring is 120°.

The four bonds of each of the "chains" were found to be coplanar within the experimental error. The coplanarity of all the atoms of the asymmetric unit was tested with respect to

the molecular plane passing through C_1, C_2 and the centre of the benzene ring. On examining the atomic coordinates with respect to the molecular axis N, (Table III) it can be seen that if another plane were chosen passing through the C_m, O, and C_1 atoms, the remaining two atoms of the "chain", i.e. C_2 and C_3, would not be distant from it by more than 0.03 A. This is due to the fact that the coordinates of C_m and O with respect to the N axis have small negative values, whereas that of C_3 is positive. In addition to being coplanar, the four "chain" bonds were found to be arranged in a zigzag fashion, the alternative bonds being almost parallel to each other. This arrangement is reminiscent of that found in aliphatic conjugated systems and it will be referred to later, when an attempt will be made to explain the results obtained.

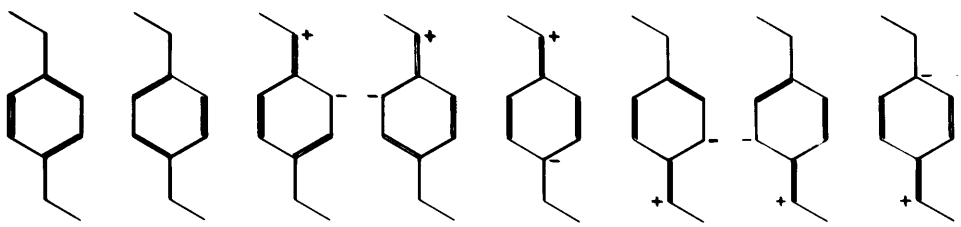
With regard to the planarity of the molecule as a whole, the results are in favour of the coplanarity of all the atoms of the molecule with the exception of the four methyl hydrogen atoms and the C_6 and C_3 atoms. The latter were found to lie 0.06 A. below and above the plane of the molecule respectively. This distance appears to be too great to be due solely to experimental error.. It also seems significant that this slight puckering of the benzene ring manifested itself at the bonds of smallest double-bond character.

With regard to the position of the methyl group, it should be added that since the C_1-O bond was found to have a

considerable amount of double-bond character a restriction of rotation of the methyl group around that bond may be expected. The structure in which it is situated in the plane of the benzene ring may be the most stable, as was indeed indicated by Pauling[37]. In his interpretation of the infra-red absorption spectra of ortho substituted phenols, he predicted that the hydrogen atom of the hydroxyl group should lie in the plane of the benzene ring. O. R. Wulf and coworkers[38] verified experimentally the above prediction and applied it to the position of the methyl group in guaiacol.

All the intermolecular distances were found to agree with the sum of the corresponding van der Waals atomic radii. This result is in agreement with the volatility of the compound and it indicates that the differences in the bond lengths are not caused by the positions of the molecules with respect to each other.

At first the following eight resonance structures were considered to contribute most to the normal state of the molecule.



I II III IV V VI VII VIII

It was assumed that these structures made equal contributions and the average double-bond character was computed for each link. These are shown as percentage double-bond character in Fig. 9a. Using the Pauling-Brockway[39] curve the corresponding bond lengths were derived and they are given in Fig. 9b.

The C_1-O bond length was calculated by means of Pauling-Brockway equation.

$$R = R_1 - (R_1 - R_2)\frac{3x}{(2x + 1)}$$

where:-

R = interatomic distance for the bond of intermediate type.

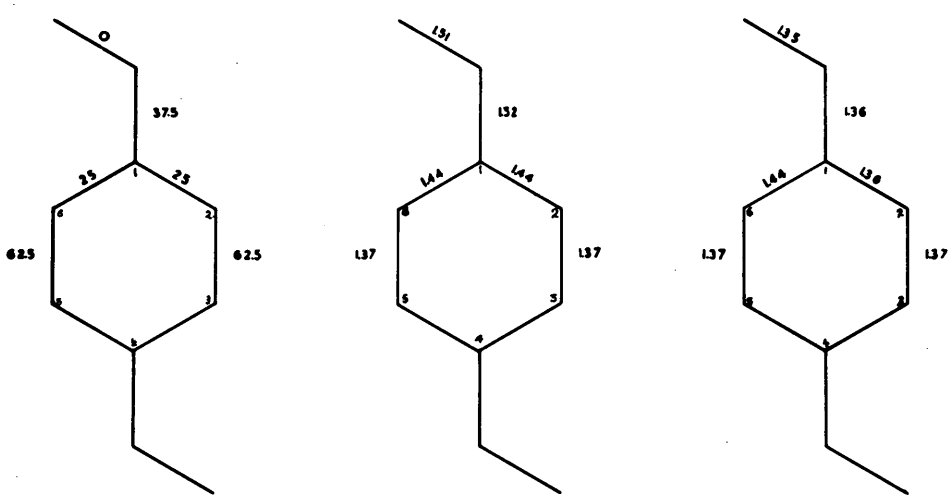
R_1 = the length of the single bond, C-O = 1.51 A. This value was obtained by adding the single covalent bond radii of the carbon and oxygen atoms. The corrected value of Schomaker and Stevenson[40] for the single bond radius of the oxygen atom (0.74 A.) was taken.

R_2 = the length of the double bond C = O, i.e. 1.215A. The double bond radii taken to give this value were: 0.665 A. for the carbon and 0.55 A. for the oxygen atom.[41]

x = the amount of the double-bond character.

For convenient comparison of the derived bond lengths with the measured values, the latter are repeated in Fig. 9c.

Fig. 9.



a b c

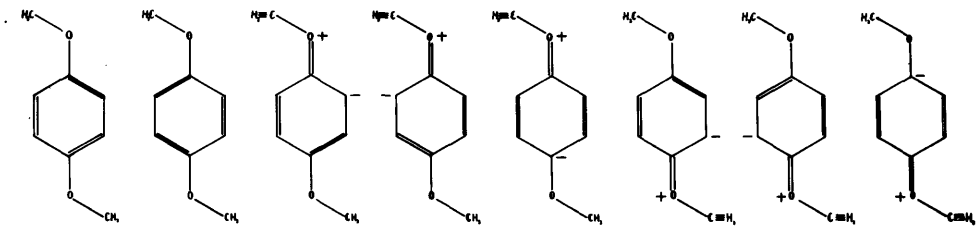
Bond orders.	Distances calculated.	Distances measured.

The C_1-C_6 and C_2-C_3 bond lengths were found to be in very good agreement with the values obtained by means of the Pauling-Brockway curve. This held also for the opposite C_3-C_4 and C_5-C_6 bonds, because the molecule possesses a centre of symmetry. This was rather an unexpected result as there was little doubt that of the above eight structures, I and II would contribute more than the remaining six, in which the charges placed on the carbon and oxygen atoms were not in agreement with the electronegative character of these atoms.

On comparison of the remaining bond distances it was found that the measured O-C_m and C_1-C_2 bond lengths were shorter than the corresponding calculated values by 0.16 A. and 0.08 A. respectively. The C_1-O bond on the other hand was 0.04 A. longer.

It should be added that if the value given by Pauling and Huggins[15] for the single bond oxygen radius (0.66 A.) was used instead of the Schomaker and Stevenson value, both the O-C_m and C_1-C_2 bonds showed shortening by 0.08 A., whereas the O-C_1 bond was found to be 0.07 A. longer than the expected value.

The consideration of the contribution made by the following structures to the normal state of the molecule affords a better explanation of the results obtained.



I II IX X XI XII XIII XIV

The structures IX - XIV differ from those considered previously only in that the first order hyperconjugation is introduced.

In addition to the type of resonance existing in conjugated structures to which C.K. Ingold[42] gave the name "mesomerism", a new type of resonance which was first known as "Baker-Nathan effect"[43] and is now referred to as hyperconjugation has appeared in various theoretical investigations. Quantum-mechanical studies[44] have also indicated the necessity of introducing the concept of hyperconjugation, and in these the three C-H bonds in a methyl group were likened to a triple bond. This similarity was emphasised by writing $-C \equiv H_3$. The $-C \equiv H_3$

although much more saturated than a true carbon to carbon triple bond, has been shown to possess a considerable conjugating power.

There are two types of hyperconjugation. First order hyperconjugation takes place when the carbon to hydrogen bonds enter into hyperconjugative resonance across the intervening C-C single bond with a second double or triple bond. Second order hyperconjugation on the other hand involves hyperconjugative resonance of the C-H bonds with other suitably placed carbon to hydrogen bonds. The effects of resonance of the first order hyperconjugation are very marked and in many cases a considerable strengthening and shortening of the acceptor bonds has been observed. The double-bond character of the donor bonds, however, was invariably found to be affected very little, only slight lengthening of these bonds being obtained.

The structures which showed the presence of hyperconjugation were found to be stabilised by the resonance energy gained from the additional resonance.

Recently the concept of hyperconjugation has been used to explain the results of several X-ray analyses. G. A. Jeffrey attributed the shortening of C-C bonds in geranylamine hydrochloride[45] and in dibenzyl[17] to the hyperconjugation process in which the methylenic electrons became partially localised in these bonds. The bond length variations in β-succinic[46], adipic[47] and sebacic[30] acids could also be explained

On this basis.

The application of this type of resonance to quinol dimethyl ether appears to explain the results obtained. The assumption that the eight structures I, II and IX - XIV, contribute to the normal state of the molecule to the same extent seems to be more reasonable than that made previously. Owing to the stabilisation by hyperconjugation, the structures IX - XIV are expected to contribute much more than the corresponding III - VIII structures, which are shown on page 55. It is difficult to say whether the structures III - VIII contribute at all, or if so, to what extent. This does not complicate however, the calculations of the double-bond character for the bonds in the molecule. The arrangement of bonds in the structure IX is the same as in the strucutre III and so on for the remaining pairs of corresponding structures. If therefore a general assumption is made that each of these pairs of structures does not contribute more or less than the Kekulé structures I or II, no further specifications are necessary and the percentage double-bond character for each bond is the same as that given in Fig. 9a. It follows, therefore, that, as before, the measured bond lengths of the benzene ring with the exception of those of the C_1-C_2 and C_4-C_5 bonds are in very good agreement with the values derived by means of the Pauling-Brockway curve. If a further assumption is made that hyperconjugation effects are propagated along the bonds of the

benzene ring, which are in the 'trans' position to the methyl groups, all the deviations of the observed bond lengths from those calculated can be accounted for. Thus, in addition to the considerable shortening of the acceptor C_m-O bonds, the C_1-C_2 and C_4-C_5 bonds would also be shortened, whereas the bonds joining the oxygen atoms to the benzene ring, being donor bonds, would be slightly lengthened.

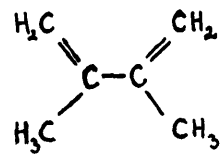
The application of the concept of hyperconjugation to quinol dimethyl ether is not complete without some consideration of additional resonance structures, in which one of the hydrogen atoms of each of the methyl groups acquires a positive charge and the C_m-O and C_1-C_2 bonds become double bonds. A more detailed investigation of this kind however, would not explain the observed bond length variations on a quantitative basis. A consideration of any unconventional structure should be withheld until more reliable results are presented by a three-dimensional X-ray analysis.

The suggested explanation of the structure of quinol dimethyl ether is not entirely unsupported by physical and chemical evidence.

Hyperconjugation is expected to stabilise the planar arrangement of the resonating bonds and this is in agreement with the results of X-ray analysis, as each of the two chains of four equal bonds (including one of the hydrogen atoms of each of the methyl groups) was found to be planar.

The benzene ring has approximately the same conjugating power as a C-C double bond[48], and since it has been shown to enter into hyperconjugative resonance with the substituent groups, e.g. in toluene, there is no obvious reason why this should not be the case in quinol dimethyl ether.

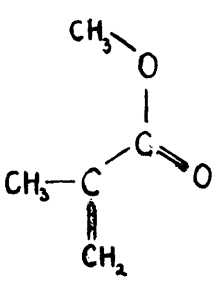
R. S. Mulliken[49] studied molecular refractivities of methyl derivatives of butadienes and came to the conclusion that the large exaltations of the end-substituted butadienes were due to hyperconjugative resonance along the "trans-trans-trans..." arrangement of their C-C and C=H_2 bonds. This suggestion was later confirmed by Hannay and Smyth[50], who studied the structure of methylated butadienes by means of dipole moment measurements. Although the structure of butadiene[51] appears to have planar and "trans" configuration, the structure of 2:3 dimethylbutadiene was shown by the above workers to have predominantly "cis" arrangement of its ethylenic bonds with respect to each other.

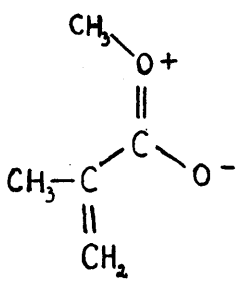


The stabilisation of this configuration may be due to the more important hyperconjugative resonance between the methyl groups and the corresponding ethylenic bonds, through C_2 & C_3 atoms. These hyperconjugating bonds are in the above structure in "trans"

position with respect to each other. Thus the configuration in which the methyl groups are "trans" with respect to the bonds of greater double-bond character appears to be more stable. The results of the X-ray analysis of quinol dimethyl ether are in agreement with the above conclusion, since the methyl groups were found in "trans" position to the C-C bonds of the benzene ring with which they are hyperconjugated.

In support of hyperconjugation taking place through the doubly linked oxygen atom, it should be added that in the case of methyl methacrylate the stabilisation of the two structures shown below may also be due to hyperconjugation.





The conjugation of an ethylenic double bond with the carbonyl group of the carbalkoxy group appears to be ineffective, and to explain this Wheland[52] suggested that this kind of resonance may interfere with a much more important resonance within the carbomethoxy group itself, which stabilises the two above structures.

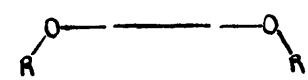
W. H. Perkin[8] measured the magnetic rotation of quinol

dimethyl ether and obtained the value 16.717. The calculated value for this compound is 10.876 and therefore the magneto-rotatory exaltation is much higher than that of benzene. (5.841 and 3.34, respectively). The magnetorotatory exaltation of benzene is caused by the conjugative resonance and in the case of quinol dimethyl ether the considerable increase of exaltation over and above the value for its benzene ring may be due to hyperconjugation. This suggestion is further supported by the fact that the magnetic rotation for quinol dimethyl ether has a higher value than expected when compared with the value obtained for veratrole. The hyperconjugative resonance in the latter is expected to be smaller owing to the less favourable position of the methyl groups.

Dr. Goodwin calculated the resonance energy of quinol dimethyl ether and obtained the value of 65 kg.-cal. This value is considerably higher than the resonance energy of benzene (41 kg.-cal.) and phenol (50 kg.-cal.) and this increase in the resonance energy may be due to hyperconjugation.

The dipole moment of a disubstituted benzene ring in para position is given by: $\mu = \mu_1 - \mu_2$, where μ_1 and μ_2 are the moments of the two substituents, provided the benzene ring is assumed to be a regular and planar hexagon. Thus in the case where the two substitutents are identical the compound should have zero dipole moment. Quinol dimethyl ether, however, has moment of 1.67 Debye units[11] as measured in benzene solution, and various explanations of this deviation from the theoretical value were suggested.

According to J. W. Williams[53] the large moment of this compound could be ascribed to the fact that the two bonds joining carbon atoms to the oxygen atom do not lie on a straight line. The molecule might have therefore, one of the two structures shown below, in which the two sidegroups are not situated in the plane of the benzene ring.



In 1930 L. Meyer[54] calculated the resultant moment of quinol dimethyl ether assuming free rotation of the methyl groups round the bonds between the oxygen and the benzene carbon atoms. He obtained the value 1.5 D.

I. Estermann[55] considered the view in which the substituent groups are assumed as fixed dipoles and the benzene ring a neutral carrier, as not at all satisfactory. He re-

garded the substituents as strongly distorted ions, which give rise to a displacement of the charges on the benzene ring and do not form a dipole unless in combination with this "distorted" residue.

There is no doubt that the rôle played by the benzene ring is important and that the contribution of possible resonance structures should be taken into account, if a quantitative explanation of the value of the dipole moment is to be offered.

The effect of hyperconjugation on the dipole moment of many compounds has been studied by C. P. Smyth and coworkers[56] and they found that an increase in moment is produced when a hydrogen atom adjacent to a double bond is replaced by a methyl group. It appears therefore that in the case of quinol dimethyl ether hyperconjugation may be responsible for the difference between the observed dipole moment (1.67 D.) and the value obtained by Meyer. (1.5 D.)

Quinol dimethyl ether has the "trans" configuration in the solid state and the high value of the dipole moment measured in benzene solution may be explained by the fact that the solute molecules are not completely rigid when subjected to the bombardment of the solvent molecules, or that the solute molecules are much distorted by forces only operative in solution, so that a stable deflection of the polar links is caused. The first explanation, which was used by Meyer, is

more likely to be correct, especially as the main difficulty, the fact that the observed value of the dipole moment is higher than the maximum calculated value of 1.5 D., appears to be solved.

Against both of the above explanations is the fact that the effect of rise of temperature should be to produce a higher value for the resultant moment due to increasing intramolecular rotation, the measurements of Hassel and Naeshagen[11] show, however, that the dipole moment of quinol dimethyl ether is not altered by a change in temperature. It is possible, however, that the rotation of the methyl groups is completely free in benzene solution even at an ordinary temperature, so that the rise of temperature would not give different values of dipole moment.

Hyperconjugation may be expected to stabilise the planar arrangement of the molecule and to prevent free rotation of the methyl groups round C_m-O as well as O-C_1 bonds. This effect however, is probably too small to prevent the rotation of the CH_3 groups on bombardment by the solvent molecules. This explanation is in agreement with the work of R. S. Mulliken[57], who concluded that the stabilisation by hyperconjugation of a plane arrangement of chains of hydrocarbons and their acids is probable, but it is doubtful whether it would be of appreciable importance quantitatively.

It seems probable that the gradual increase in the

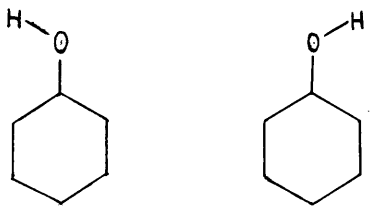
dipole moment value for dimethyl ethers of catechol, resorcinol and quinol (1.31, 1.59 and 1.67 D. respectively) may be due to the fact that in the latter compounds more C-C bonds of the benzene ring may be involved in the hyperconjugative resonance, leading to a greater separation of charges.

The results of the crystal analysis of quinol dimethyl ether appear to elucidate the infra-red spectrum of guaiacol.

O. R. Wulf and U. Liddel[58] studied the infra-red absorption spectra of several aromatic compounds containing hydroxyl groups. Their work has been carried out in carbon tetrachloride solution. They found that all these substances showed a characteristic absorption, which they believed to be due to vibrations of the phenolic hydrogen to and from the oxygen atom to which it is linked. They have also presented the evidence for the existence of measurable influence on this absorption by coupling of the hydroxyl group with an adjacent group in the molecule. Such influence consisted in pronounced frequency shifts and often splitting of the peak into two components.

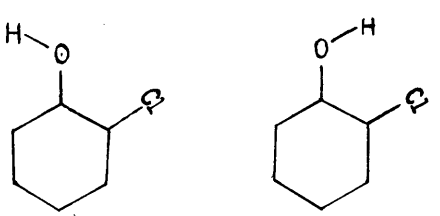
These results were interpreted by Linus Pauling[37] who arrived at the following conclusions regarding the structure of phenol, o-chlorophenol and catechol.

In the case of phenol only one absorption peak due to the hydroxyl group was obtained at frequency 7050 $cm.^{-1}$ The double-bond character of the C-O bond causes the hydrogen atom to lie in the plane of the rest of the molecule. The phenol molecule can thus assume either of the two configurations.



These two forms are equivalent and therefore only one absorption peak is expected.

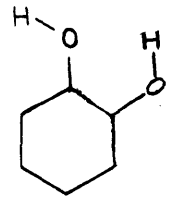
O-chlorophenol gave two peaks, one at 7050 $cm.^{-1}$ and the other at 6910 $cm.^{-1}$, the area of the latter being about ten times that of the former. Pauling attributed this result to the fact that o-chlorophenol in carbon tetrachloride solution consists of about 91% "cis" and 9% "trans" molecules.



trans cis

The "cis" form is stabilised by the interaction between H and Cl and it gives rise to the larger peak at the lower frequency. The peaks are well resolved, showing that molecules with intermediate configurations are not present in appreciable amounts.

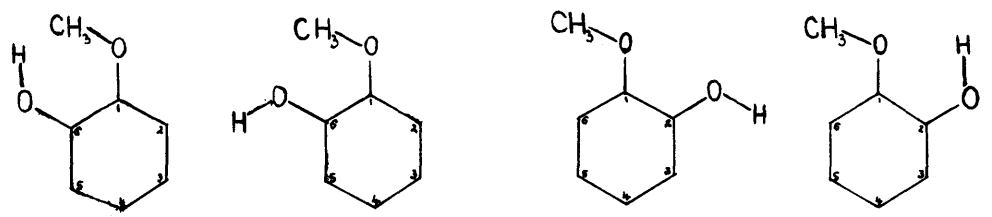
The infra-red spectrum of catechol showed two nearly equal peaks, one at the frequency of the OH group of phenol and the other at a lower frequency (7060 $cm.^{-1}$ and 6970 $cm.^{-1}$, respectively). Pauling suggested that catechol has the structure in which one hydroxyl group is "cis" and the other "trans" with respect to each other.



cis -trans

Each of these hydroxyl groups of this configuration gives rise to an absorption peak, the "cis" OH being responsible for the peak at the lower frequency owing to the interaction between its hydrogen atom and the oxygen atom of the "trans" group. If any of the other possible configurations were present to an appreciable amount the absorption peaks would not be equal.

The effect of ortho substitution on the absorption of the hydroxyl group of phenol in the infra-red was further studied by O. R. Wulf, U. Liddel and S. B. Hendricks[38], and they found that all the examined spectra appeared to possess characteristics which are strikingly in accord with Pauling's interpretation. Of special interest is the infra-red spectrum of guaiacol which showed only one sharp OH absorption peak at a slightly lower frequency than the one given by the "cis" peak of catechol. (6930 cm.$^{-1}$). This result led Wulf and his coworkers to the conclusion that out of the four possible configurations given below, the fourth one represents the structure of this compound.



1-cis 2-trans 3-trans 4-cis

Of the two "cis" forms the first one was considered to be unstable on account of the repulsion of similarly charged hydrogen atoms.

The accepted configuration possesses the OH group in "cis" position with respect to the "trans" OCH_3 group and was expected to be stabilised by the attraction of the proton of the hydroxyl group by the dipole moment of the methoxy group. The guaiacol absorption peak is, however, at a considerably

higher frequency than the "cis" peak shown by the compounds with the iodine or bromine atom in the ortho position to the OH group. This indicated that the stabilising effect in guaiacol is not so great as in the compounds stabilised by the halogen-hydrogen interaction. In the case of halogen derivatives the "trans" form was found to be present to an appreciable amount, whereas the spectrum of guaiacol did not show any presence of the "trans" configuration in spite of the fact, that the stabilising effect appeared to be smaller.

These results led Wulf and his coworkers to the conclusion that the "cis" form of guaiacol is more stable than indicated by the frequency of its OH absorption peak, i.e., the greater energy difference between the "cis" and "trans" forms of the hydroxyl group of guaiacol as compared with the corresponding energy difference in halogen compounds did not manifest itself in a lowering of the frequency of the OH absorption. This appeared to be possible as the form of the potential curve of the vibrating hydroxyl group was expected to be different in the case of guaiacol from that in the halogen compounds owing to the different nature of the attraction of the hydrogen atom.

Their alternative explanation was that there was a considerable amount of the "trans" form present, but that the difference in the absorption coefficients for the two forms have led to the formation of the "cis" absorption peak only.

This interpretation was, however, in contrast to that presumed to be true in the case of catechol.

In quinol dimethyl ether the C-C bond of the benzene ring, which is "trans" to the C-O bond of the methoxy group, was found to possess greater double-bond character than the C-C bond in the "cis" position and a qualitative explanation of this has been suggested.

It appears probable that in guaiacol hyperconjugation is also taking place and that the resonance effects are propagated along the C_1-C_2 bond of the benzene ring in a way similar to that in quinol dimethyl ether. As a result of this, it is possible that the OH group may be more likely to be attached to the C_2 than to the C_6 carbon atom of the benzene ring. If this is assumed to be the case, only the third and the fourth configuration of guaiacol, shown on page 71, remain to be considered. They differ only in the position of the hydrogen atom with respect to the methoxy group. There is no doubt, that the fourth"cis" form is stabilised by the attraction between the hydrogen atom of the OH group and the oxygen atom of the methoxy group, but this stabilising effect must be small, not only because it manifested itself only in a slight shift of the frequency of the OH absorption peak, but also, as Gordy[59] demonstrated, the proton attraction character of the oxygen atom in aromatic ethers is quite low compared with that in aliphatic ethers. In addition, according to

Pauling[60] the O-H...O hydrogen bond formed in guaiacol is weak, because of the unfavourable steric conditions. The fact, that the resonance structures of guaiacol in which hyperconjugation is taking place are expected to contribute to the normal state of the molecule to a considerable degree, also supports this suggestion, since they involve a positively charged oxygen atom of the methoxy group.

The absence of the "trans" form of guaiacol, however, points to a considerable stabilisation of the "cis" form, in addition to that by the hydrogen bond formation.

In quinol dimethyl ether the methyl group was found to occupy a definite position with respect to the distorted benzene ring. There is little doubt that the carbon-carbon bonds in the benzene ring of guaiacol are also varying in length and by analogy it is reasonable to expect that the position of the hydrogen atom in the "cis" form may be determined by the electron distribution of the benzene ring. This explanation agrees well with the infra-red spectrum of guaiacol as the frequency of its OH absorption peak is not expected to be lowered by this kind of stabilisation.

REFERENCES.

1. Sutton and Brockway, J. Amer. Chem. Soc., 1935, 57, 473.
2. Bennett, Trans. Faraday Soc., 1934, 30, 853.
3. Bennett and Glasstone, Proc. Roy. Soc., 1934, A, 145, 71.
4. Sutton and Hampson, Trans. Faraday Soc., 1935, 31, 945.
5. Robertson, Proc. Roy. Soc., 1933, A, 140, 79.
   Robertson, Proc. Roy. Soc., 1933, A, 142, 659.
   Robertson, Proc. Roy. Soc., 1933, A, 142, 674.
   Robertson, J., 1939, 1324.
6. Robertson, Acta Crystallographica, 1948, 1, 3.
7. Reis and Zimmermann, Z. physikal.Chem., 1922, 102, 332.
8. Perkin, J., 1896, 69, 1240.
9. Baly and Ewbank, J., 1905, 87, 1353.
   Baly and Rice, J., 1912, 101, 1481.
   Franzen, J. pr. Chem., 1918, 2, 98, 79.
10. Stohmann, Rodatz and Herzberg, J. pr. Chem., 1887, 35, 22.
11. Hassel and Naeshagen, Z. physikal. Chem., 1930, B, 8, 357.
12. International Tables for the Determination of Crystal Structure, 138.
13. Robertson, Proc. Roy. Soc., 1936, A, 157, 79.
14. Palin and Powell, J., 1947, 208.
15. Pauling and Huggins, Z. Krist., 1934, 87, 205.
16. Pauling, The Nature of the Chemical Bond, (Cornell University Press), 1945, 168.

17. Jeffrey, Proc. Roy. Soc., 1946-47, A, 188, 222.

18. Pauling, The Nature of the Chemical Bond, 1945, 189.

19. Vermeulen, Rec. trav. chim., 1906, 25, 28.

20. Harthshorne and Stuart, Crystals and the Polarising Microscope, 137.

21. Harthshorne and Stuart, Crystals and the Polarising Microscope, 143.

22. Buerger, X-Ray Crystallography, (Wiley & Sons), 1942, 179.

23. Robertson, J. Sci. Instr., 1943, 20, 175.

24. Lonsdale, Structure Factor Tables, (Bell & Sons), 41.

25. Bragg and Lipson, Z. Krist., 1936, A, 95, 323.

26. Robertson, Progress in Physics, 1938, 4, 332.
Robertson, Phil. Mag., 1936, 21, 176.

27. Beevers and Lipson, Proc. Physical Soc., 1936, 48, 772.

28. Robertson, J. Sci. Instr., 1948, 25, 28.

29. Robertson, Proc. Roy. Soc., 1935, A, 150, 110.

30. Robertson, and Morrison, J., 1949, 993.

31. Booth, Proc. Roy. Soc., 1947, A, 190, 482.

32. Robertson and Sinclair, unpublished.

33. Lukesh and Pauling, Fourth Annual Spring Meeting of the Crystallographic Society of America.

34. Robertson and Abrahams, unpublished.

35. Robertson and Abrahams, Nature, 1947, 160, 569.
Robertson and Abrahams, Acta Crystallographica, 1948, 1, 252.

36. Robertson and White, Proc. Roy. Soc., 1947, A, 190, 329.

37. Pauling, J. Amer. Chem. Soc., 1936, 58, 94.

38. Wulf, Liddel and Hendricks, J. Amer. Chem. Soc., 1936, 58, 2287.

39. Pauling and Brockway, J. Amer. Chem. Soc., 1937, 59, 1223.

40. Schomaker and Stevenson, J. Amer. Chem. Soc., 1941, 63, 37.

41. Pauling, The Nature of the Chemical Bond, 1945, 169.

42. Ingold, Nature, 1934, 133, 946.

43. Baker and Nathan, J., 1935, 1844.

44. Mulliken, J. Chem. Physics, 1939, 7, 339.
Mulliken, Rieke and Brown, J. Amer. Chem. Soc., 1941, 63, 41.

45. Jeffrey, Proc. Roy. Soc., 1944-45, A, 183, 388.

46. Robertson and Morrison, J., 1949, 980.

47. Robertson and Morrison, J., 1949, 987.

48. Pauling and Sherman, J. Chem. Physics, 1933, 1, 679.

49. Mulliken, J. Chem. Physics, 1939, 7, 363.

50. Hannay and Smyth, J. Amer. Chem. Soc., 1943, 65, 1931.

51. Mulliken, J. Chem. Physics, 1939, 7, 131.
Mulliken, Rev. Mod. Physics, 1942, 14, 265.
Schomaker and Pauling, J. Amer. Chem. Soc., 1939, 61, 1769.

52. Wheland, The Theory of Resonance and its Application to Organic Chemistry, (Wiley & Sons), 74.

53. Williams, Physikal. Z., 1928, 29, 683.

54. Meyer, Z. physikal. Chem., 1930, B, 8, 27.

55. Estermann, The Dipole Moment and Chemical Structure, edited by Debye, 1931, 31.

56. Hurdis and Smyth, J. Amer. Chem. Soc., 1943, 65, 89.
Hannay and Smyth, J. Amer. Chem. Soc., 1946, 68, 244.
Hannay and Smyth, J. Amer. Chem. Soc., 1946, 68, 1357.
57. Mulliken, J. Chem. Physics, , 1939, 7, 351.
58. Wulf and Liddel, J. Amer. Chem. Soc., 1935, 57, 1464.
59. Gordy, J. Chem. Physics, 1940, 172.
60. Pauling, The Nature of the Chemical Bond, 1945, 385.

THE CRYSTALLITE ORIENTATION

IN DIFFERENT GRADES OF MANILA AND SISAL FIBRES.

SUMMARY.

Two X-ray photographs, one at the root, and the other at the tip were taken for many fibres of different grades of Manila, Davao and sisal. The orientation of the cellulose structural units was studied in terms of the spiral angle values measured from each photograph.

All fibres showed an increase in crystallite orientation from the root to the tip of the fibre accompanied by an increase in the tensile strength.

The partially-cleaned Manila fibres showed lower tenacity (gm/denier) values than were expected from the small spiral angle values. This is probably due to the presence of an increased amount of non-cellulose material.

Davao fibres showed smaller orientation and were generally weaker than the corresponding Manila hemps grown in other provinces.

Sisal fibres had much greater spiral angle values and smaller tensile strengths than Manila hemps.

INTRODUCTION.

The crystalline structure of native cellulose which constitutes about 74% of content of Manila and 73% of sisal fibres[1] has been studied extensively by many workers. The size and the shape of the crystalline submicroscopic areas, called micelles or crystallites have also been studied and many theories have been advanced in connection with the nature of the crystallites. A detailed survey of the X-ray work has been given by W. A. Sisson[2] in the 5th volume of "High Polymers".

Manila and sisal X-ray photographs show small diffraction arcs on the equators, which arise from planes parallel to the fibre axis. The lengths of the arcs give measure of the angle between the crystallite long ('b') axes and the fibre axis. In Manila and sisal the crystallites lie along spiral paths about the fibre axis. From the lengths of the arcs on X-ray photographs taken with the fibres perpendicular to the X-ray beam the spiral angle values can be estimated. The spiral orientation has been confirmed by taking X-ray photographs of stretched Manila and sisal fibres. A decrease in length of the diffraction arcs, i.e. a decrease of angle between the spiral and the fibre axis was observed.

Manila fibres are composed of bundles of cells ranging from 3 - 12 mm. in length and 16 - 32 microns in width.[3]

Sisal cells are considerably shorter varying in length from 1.5 to 4 mm.[4] Microscopic examination of many specimens of Manila and sisal showed that their cells are parallel to one another.

The cell walls of Manila and sisal fibres are comparatively thin and it was not possible to examine the fibril orientation in the cell walls and correlate it with the spiral angle measurements. This was done for ramie[5] and cotton[6] fibres and it has been possible to account completely for the orientation observed in the X-ray diagrams on the basis of the fibril orientation. It appears probable that this is also the case with Manila and sisal fibres, as on swelling of the specimens with zinc chloriodide solution and heating for a few minutes spiral markings were observed[1].

The intensity distribution on 101, $10\bar{1}$ and 002 diffraction rings was exactly the same in all photographs of Manila and sisal fibres. This is in agreement with the work of W. A. Sisson[5], who concluded that these fibres have non-selective spiral orientation, i.e. their crystallites have a random rotation around their own axes.

Some of the X-ray photographs of Manila and sisal fibres are shown on page 4 and it can be seen that four intensity maxima were obtained on each of the diffraction rings when the spiral angle is large and the deviation from the spiral angle small.

The deviation from the spiral angle is due to the cylindrical form of fibres, since the fibrils in the portion of the cell wall parallel to the X-ray beam diffract at the equator rather than at an angle corresponding to the spiral angle.

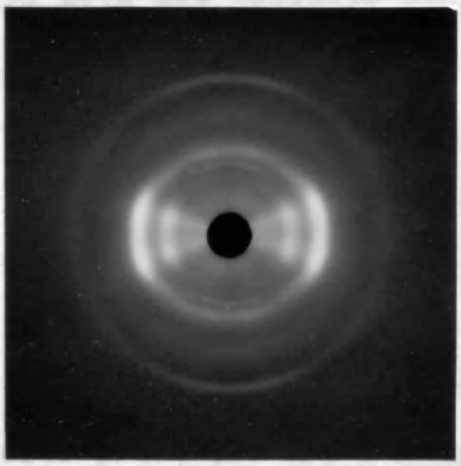


Fig. 1. Manila S2 (root).

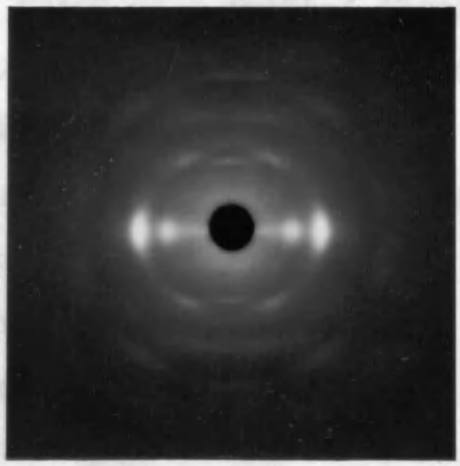


Fig.2. Manila S2 (tip).

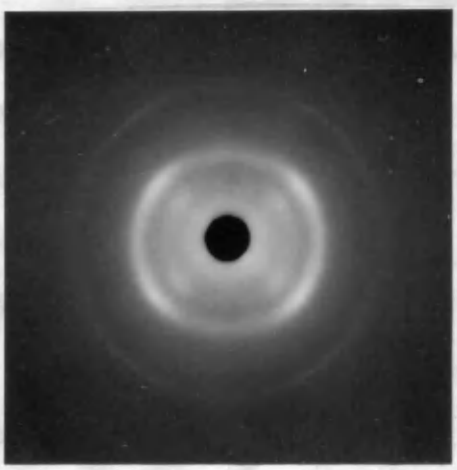


Fig.3. Sisal R (root).

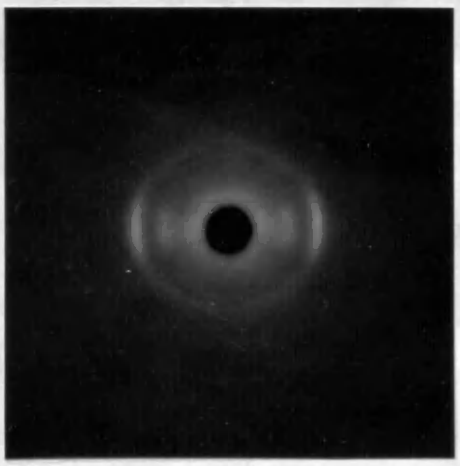


Fig.4. Sisal R (tip).

EXPERIMENTAL.

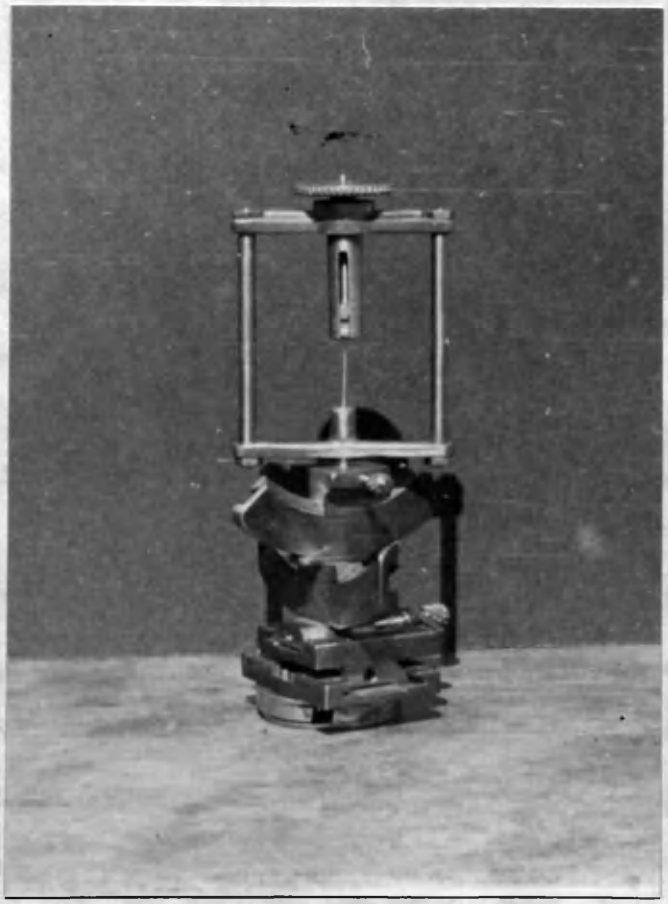
All the photographs were taken with the fibres set perpendicular to the X-ray beam and without rotating the fibres. Quarter-plate films were used, the film-holder being attached to an open spectrometer. The distance of the film from the fibre axis was adjusted carefully by means of a pointed steel rod exactly 3 cm. long. A $\frac{1}{2}$ mm. collimator was used for most of the photographs and precautions were taken to exclude all the X-ray radiation other than that passing through the collimator and diffracted by the specimens.

In most of the cases the fibres were found to be too flexible to be mounted directly on a pair of arcs and a special frame for holding them had to be constructed. The design of this frame is shown in Fig. 6 and it can be compared with its photograph in Fig. 5 .

The frame was fitted on a pair of arcs, so that the fibre could be set perpendicular to the X-ray beam. The frame itself had a built-in nut capable of rotation and a feathered, screwed rod shown on the left of the drawing. By rotating the nut on top of the frame this rod could have only translational motion due to the feathers moving in fixed slots. The ends of the fibre were screwed to the lower part of the frame and to the lower end of the screwed rod. Since the rod was capable only of translational motion, the frame could be

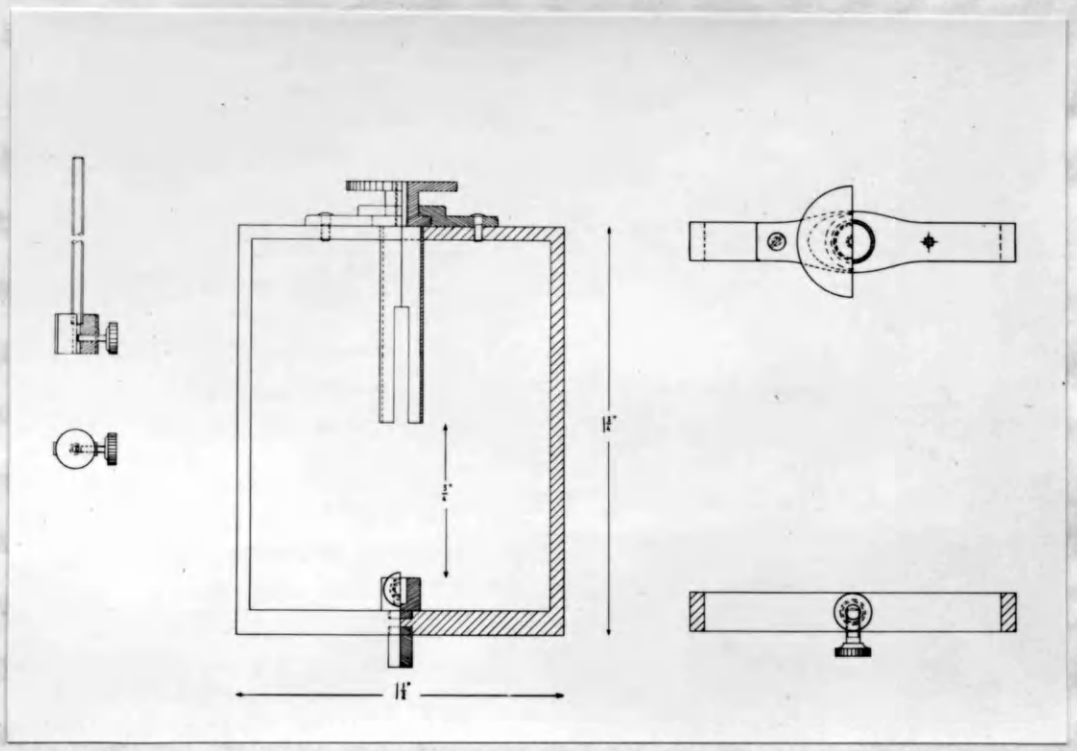
used not only for holding the fibres but also for stretching them, as no twisting of the fibres was possible. The frame was carefully calibrated and the amount of stretching could be measured accurately, since one quarter of a turn of the large top nut stretched the fibre by a fraction of a mm. only.

Fig. 5.



Frame for holding and stretching the fibres.

Fig. 6.



Design of the frame for holding and stretching the fibres.

The X-ray beam was not strong enough for taking photographs of Manila and sisal fibres. To decrease the time of exposure to four or five hours, it was necessary in many cases to take a few fibres, occasionally as many as six, and stick them together by means of "Durofix" thinned with amyl acetate solution. Care was taken to fix the fibres, so that their axes were parallel to one another. The amount of error introduced by this method was very small, this was confirmed

by the fact that on several occasions the spiral angle measurements of photographs of two bundles of fibres of the same grade did not differ appreciably from each other.

At first the crystallite orientation was estimated by measuring the length of the 002 diffraction arc. This method was however abandoned and the more accurate and simple method of reading the spiral angle directly by means of a protractor was used. This was done by placing two sheets of cellophane between the photograph and the protractor, each with a thin, scratched line. These were then held firmly in such a way that these two lines crossed each other at the centre of the photograph enclosing both arcs on each of the 002, 101 and $10\bar{1}$ diffraction rings. This method eliminated the small errors that might have existed in the slight variations of distance between the axis of the fibre and the film. Also, since the density distribution curves for the (101), ($10\bar{1}$) and (002) planes were the same, the spiral angle could be estimated more accurately by taking the lengths of arcs of all the above planes into account rather than only that of the (002) plane. This was important as the intensity of the (002) reflection varied considerably in different photographs.

At least six measurements were made for each X-ray photograph and the average values obtained were then divided by two.

The more elaborate quantitative measurements which

could have been carried out by means of a microdensitometer[7] were considered to be unnecessary, since slight variations were shown by different fibres of the same grade even at the same distance from the root of the fibre. Although the accuracy of the measurement of each individual photograph would be greater, it could not be applied to the grade of any fibre as a whole.

The Measurements of the Tenacity of the Fibres.

These measurements were carried out at Mr. Mattinson's laboratory at Gourock Ropework Co. Ltd.

Fifty samples of each grade were chosen and 1½ " lengths were cut at the root and at the tip. Each group of fifty roots and tips was then weighed and the average denier, i.e. the weight in grams of 9000 metres of the fibre was calculated.

The Fibre Testing Machine was used for the measurement of the breaking strength of each sample. Samples were broken ½" between the grips and care was taken to break them as near the root or the tip of the fibre as possible.

Some of the coarse fibres had to be broken on the Textile Yarn Testing Machine. The results obtained were however not nearly so accurate as those obtained with the Fibre Testing Machine and were not correlated with the spiral angle measurements.

RESULTS.

MANILA FIBRES.

		Spiral angle.
Borneo B.	root	11.5°
	tip	4.1°
Borneo C.	root	15.3°
	tip	4.1°
Manila C.D.	root	4.4°
	tip	2.8°
Manila E.	root	10.1°
	tip	2.9°
Manila F.	root	7.0°
	tip	2.5°
Manila S.2.	root	16.5°
	tip	3.9°
Manila G.	root	18.8°
	tip	3.2°
Manila H.	root	10.8°
	tip	3.9°

		Spiral angle.
Manila I.	root	8.9°; 7.4°
	tip	5.2°; 4.4°
Manila J.1.	root	8.7°
	tip	2.8°
Manila K.	root	6.6°
	tip	5.3°
Manila L.2.	root	8.3°
	tip	4.8°
Manila M.2.	root	3.5°
	tip	2.7°

DAVAO FIBRES.

	Spiral angle.	Average Breaking Strength. (gms.)	Denier.	Tenacity. (gms/denier.)
Davao C.D.				
root	5.4°	1679.76	316.1	5.31
tip	4.0°	670.68	111.3	6.03
Davao F.				
root	10.5°			
tip	5.0°			
Davao S.2.				
root	25.7°	2193.36	443.7	4.94
tip	2.4°	713.32	65.5	10.89
Davao G.				
root	29.4°	1922.2	430.4	4.47
tip	3.6°	1055.42	173.4	6.09
Davao H.				
root	13.9°	2504.0	564.1	4.44
tip	4.0°	1059.4	133.8	7.92
Davao I.				
root	14.8°	2881.95	519.9	5.54
tip	3.9°	1305.64	181.9	7.18
Davao J.1.				
root	20.4°	2161.72	484.0	4.47
tip	4.2°	931.56	80.4	11.58

	Spiral Angle.	Average Breaking Strength. (gms.)	Denier.	Tenacity. (gms/denier.)
Davao J.2.				
root	7.2°	2120.32	295.0	7.19
tip	4.9°	1141.24	101.0	11.30

MANILA HEMPS - GRADING DEFINITIONS.

Grade.	Colour.	Texture.	Cleaning.	Length.
B. 100% over Good Current.	White.	Soft.	Excellent.	
C. 50% over Good Current.	Very light ivory yellow.	do.	do.	3/7' or under.
D. Good Current.	Ivory yellow.	do.	do.	do.
E. Midway.	Very light ochre & ivory yellow.	do.	do.	do.
F. 25% over Fair Current.	Light ochre or very light brown.	Fine to Medium.	do.	do.
S2. Streaky No.2.	Ochre light brown. Light red.	Soft.	do.	do.
G. Soft Seconds.	Dark brown. Light green.	Medium soft.	Good.	Short to 7'.
H. Soft Brown.	Brown, dark brown nearly black.	Soft.	do.	do.
I. Fair Current.	Very light brown.	Medium soft.	do.	3/7' or more.
J1. Superior Seconds No.1.	Light brown or dingy white.	do.	Good/ Fair.	do.

Grade.	Colour.	Texture.	Cleaning.	Length.
J.2. Superior Seconds No.2.	Dingy light brown or yellow.	Medium to bold.	Fair.	3/7' or more.
K. Medium Seconds.	Dingy light brown or yellow.	Medium.	do.	Short to 7'.
L2. Coarse Seconds.	Dingy brown or yellow.	Hard.	Coarse.	3/7' or more.
M2. Coarse Brown.	Dark brown - some nearly black.	Hard.	do.	Short to 7'.

Cleaning.

Excellent. - Pure fibre with little or no pulp attached.

Good. - Fine soft strips sometimes intermixed with pure fibre.

Fair. - Strips with little or no pure fibre in evidence.

Coarse. - Strips ranging from 1½ to 3 mm. in width.

SISAL FIBRES.

	Spiral Angle.	Average Breaking Strength. (gms.)	Denier.	Tenacity. (gms/denier.)
Sisal 1P.				
root	17.0°	726.6	227.0	3.20
tip	12.3° 11.4°	596.48	122.4	4.87
Sisal 2. (Himo)				
root	26.0°	783.72	191.5	4.09
tip	9.8°	538.48	57.5	9.36
Sisal 3L. (Masimru)				
root	29.8°	1124.02	283.2	3.97
tip	10.7°	755.06	111.0	6.80
Sisal 3L. (Amsawa)				
root	24.0°	1738.32	598.6	2.90
tip	12.9° 12.8°	466.66	127.9	3.65
Sisal 3. (Marran 5)				
root	22.5°	824.68	236.0	3.49
tip	7.8°	330.4	89.0	3.71
Sisal R.				
root	38.6°	804.2	255.9	3.14
tip	9.7°	474.28	131.0	3.62

SISAL - GRADING DEFINITIONS.

Grade.

1. Length from 3' with average of 3'6". Free from defective decortication. Properly brushed. Free from tow, bunchy ends, knots and harshness. Colour - creamy white to cream.

2. Same as 1, but length from 2'6" upwards.

3L. Length from 3' upwards, consisting of brushed fibre that does not conform to Grade 1 or 2. Although minor defects in colour and cleaning are allowable it must be free of barky or undecorticated fibre and knots.

3. Same as 3L but length from 2' upwards.

R. Fibre that does not conform to the above mentioned grades as regards length, colour and cleaning, but minimum length is 2'.

DISCUSSION OF RESULTS.

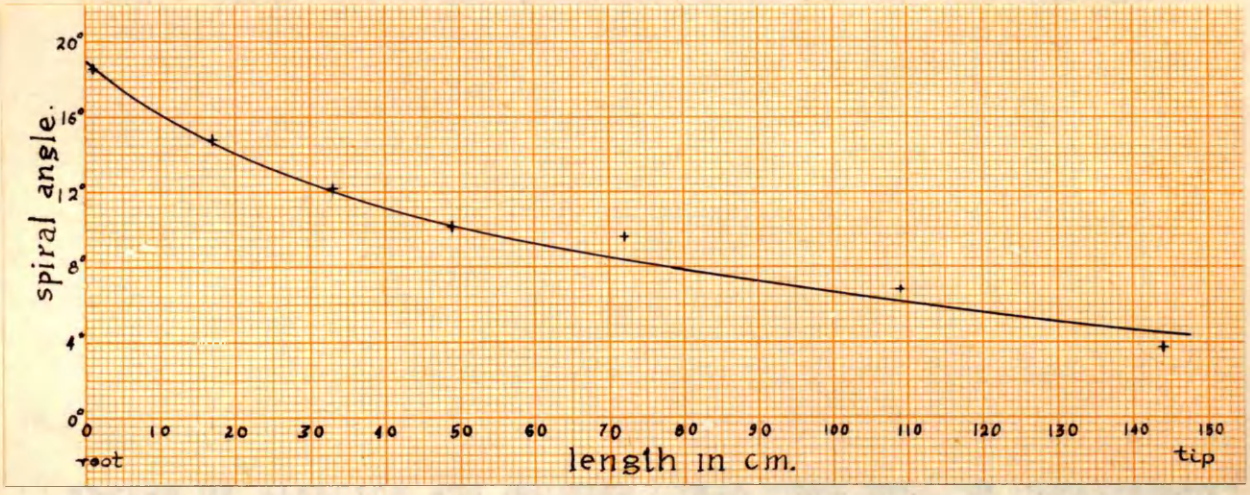
The error in the values of the spiral angle probably lies within $\pm 1.5^{\circ}$. The values of the tenacity, (gm/denier) which are given together with the values of the spiral angle can be used for rough comparison only. It can be seen that the increase of orientation is connected with the increase of tensile strength of fibres. This is in agreement with the work done previously on cotton fibres.[8]

An attempt was made to study quantitatively the relationship between tensile strength and orientation: it seems that the "tenacity/spiral angle" curve for Manila hemp differs considerably from that for sisal fibres. Further investigation on these lines must, however, await more accurate tensile strength measurements.

For each of the Manila and sisal fibres the spiral angle values at the root were found to be invariably greater than those at the tip. In many cases this difference in orientation of crystallites with respect to the fibre axis was very great and a corresponding considerable difference in the tensile strength was observed. Two such specimens were chosen, Manila G and sisal 3L (Masimru) and the change of orientation towards the tip of the fibre was studied. Several X-ray photographs were taken of each fibre at different points along the length between the root and the tip.

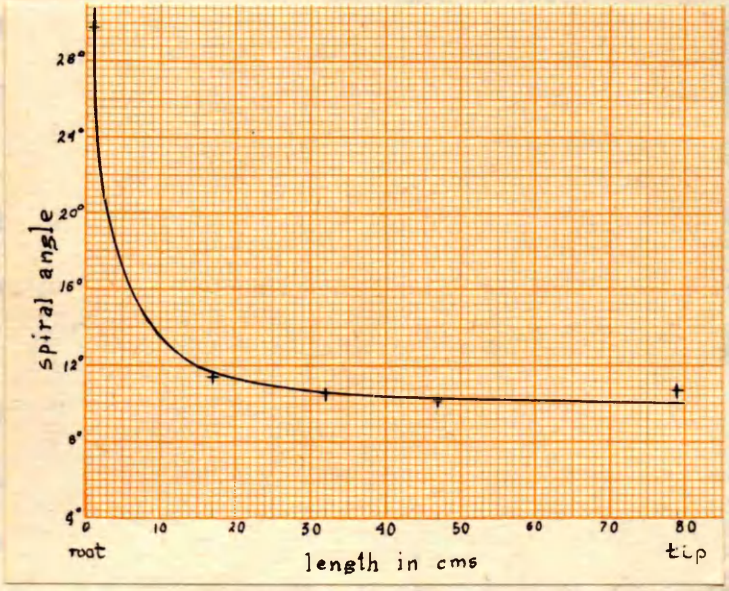
The two "orientation/length of the fibre" curves which were obtained are shown in Fig. 7 and 8.

Fig. 7.



Relationship between orientation and length of Manila G fibre.

Fig. 8.



Relationship between orientation and length of sisal 3L fibre.

The shape of the curve for the Manila fibre is quite different from that for sisal. The former shows a gradual increase in orientation along the fibre towards the tip, whereas in the case of sisal there is a great decrease of the value of spiral angle within the first 15 cm. from the root end of the fibre, the spiral angle then approximating to a constant value. This considerable difference in the shape of the curve for the two fibres may be a general characteristic for the two types of hemp, Manila and sisal. Before any importance can be attached to this suggestion, however, further investigation would be required.

Manila and sisal hemps are graded according to degree of cleaning and colour. (see "The Grading Definitions" given at the end of Manila and sisal orientation and tensile strength measurements). Relative strengths of Manila hemps were given in the literature[9] and these show a decrease along the grading series, so that the partially-cleaned fibres are considerably weaker than the well-cleaned hemps.

Many of the tenacity measurements of Manila were obtained using the Textile Yarn Testing Machine and were not accurate enough for correlation with the crystallite orientation. They showed however, with a few exceptions, the above mentioned decrease in strength along the grading series. Of special interest is the fact that according to the spiral angle values Manila G should be slightly weaker at the root

than Manila S2. The tenacity measurements showed however, that of the two fibres Manila S2 is much weaker. This is probably due to the presence of non-cellulose material which gives rise to a relatively large value of denier. This is likely to be the cause of the smaller tensile strength values for the partially-cleaned fibres, Manila L2, M2, and K. High values were expected from the high crystallite orientation in these fibres.

The spiral angle measurements together with the tenacity values for Davao and sisal fibres give the first full and accurate account of the variation of these two qualities in different grades.

Davao fibres are generally acknowledged to be stronger than the corresponding Manila hemps grown in other provinces.[10] The values of the spiral angle for Davao fibres at the root and at the tip, on the other hand, are generally greater than the corresponding values for Manila, indicating smaller tensile strength. The Davao fibres are generally harder in texture and bolder in size and therefore their breaking strength values as compared with those of Manila may be in many cases much greater. There is little doubt, however, that the tenacity values, which take the weight of the fibre into account, are lower for Davao fibres than for the corresponding Manila fibres.

On comparison of the results for Manila and sisal

fibres, it can be seen that the latter have generally smaller orientation of the cellulose structural units at the root and at the tip of the fibre. The tensile strength measurements are in agreement with this conclusion as the tenacity values for sisal are comparatively small. The fact that sisal fibres may not have the gradual increase of crystallite orientation from the root to the tip of the fibre, but have the better 'tip' spiral angle value throughout most of their length may make these fibres much more valuable than can be inferred from the comparison of root and tip spiral angle and tenacity values alone.

REFERENCES.

1. Castle and White, J. Text. Inst., 1942, 33.
2. Sisson, High Polymers, 1943, 5, 203.
3. Matthews, The Textile Fibers, (Wiley & Sons), Fourth edition, 812.
4. Matthews, The Textile Fibers, Fourth edition, 818.
5. Sisson, Ind. Eng. Chem. (Anal.), 1935, 27, 51.
6. Sisson, Contrib. Boyce Thompson Inst., 1938, 9, 239.
7. Sisson and Clark, Ind. Eng. Chem. (Anal.), 1933, 5, 296.
8. Sisson, Textile Research, 1937, 7, 425.
9. Matthews, The Textile Fibers, 1947, 372.
   Weindling, Long Vegetable Fibers, (Columbia University Press), 1947, 50.
10. Weindling, Long Vegetable Fibers, 1947, 49.